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STUDIES ON THE CHEMISTRY OF RHENIUM. PART I. COMPLEX OXALATES OF QUADRIVALENT RHENIUM

By Debabrata Sen and Priyadaranjan Ray

It has been found that the tetrapositive rhenium combines with oxalic acid to form a complex acid, aquo-trihydroxo rhenioxalic acid, H $[(OH)_3.Re.C_2O_4.H_2O]$, which slowly changes in aqueous solution into the dibasic form, $H_2[(OH)_4.Re.C_2O_4]$, tetrahydroxo rhenioxalic acid. The values of the two successive dissociation constants, k_1 and k_2, as determined by potentiometric titration, are 7.94×10^{-3} and 1.02×10^{-5} respectively. Alkali, alkaline earth and many heavy metal salts of both the forms of the acid have been described. Measurement of the magnetic susceptibility of the disodium salt gives a diamagnetic value. This is rather unusual for quadrivalent rhenium with an odd number of electrons, either in a simple or a complex compound. The phenomenon seems to suggest Re—Re metallic bonds.

Besides the well known and the most stable septivalency, rhenium exhibits a fairly stable stage in its quadrivalent condition. In this state it gives rise to complex halides of the type, $R_2[Re\,X_6]$ where R = a univalent metal atom and X = Cl, Br or I (Briscoe, Robinson and Stoddart, *J. Chem. Soc.*, 1931, 2263; Krauss and Dahlmann, *Ber.*, 1932, **65B**, 877; Krauss and Steinfeld, *Ber.*, 1931, **64B**, 2552; Schmid, *Z. anorg. Chem.*, 1933, **212**, 187). The metal also forms fairly stable oxycyanides in its quinquevalent state (Klemm and Frishmuth, *Z. anorg. Chem.*, 1937, **230**, 215). It was therefore expected that the element might also form complex oxalates, particularly in view of the occurrence of similar oxalates formed by the neighbouring elements tungsten and osmium. Experiments carried out with this end in view have led to the successful preparation of complex oxalates of quadrivalent rhenium.

By the dissolution of freshly prepared ReO_2 in oxalic acid, a complex acid of composition, $ReO.C_2O_4.3H_2O$, was obtained. The three molecules of water could not be removed without the decomposition of the substance itself. It can therefore be represented as a complex acid of the constitution $H[Re.(OH)_3.C_2O_4.H_2O]$ or $H_2[Re.(OH)_4.C_2O_4]$. This is supported by the potentiometric titration of its aqueous solution by an alkali, which indicates that the acid behaves primarily as a monobasic one, but gradually changes into a dibasic form. In solution it therefore exists in equilibrium between the two forms as shown below :

$$H[Re.(OH)_3.C_2O_4.H_2O] \rightleftarrows H_2[Re.(OH)_4.C_2O_4]$$

On titration with alkali, the neutralisation occurs before two equivalents of alkali are added for each molecule of the acid ; but if the solution is allowed to stand, the p_H continues to fall due to the formation of the dibasic form. This is evident also from the p_H—neutralisation curve, which shows a sharp rise on rapid titration before second neutralisation point, indicating that the neutralisation of the second hydrogen ion is not an instantaneous process. If, however, the titration is slowly carried out allowing sufficient time for the attainment of equilibrium after each addition of alkali, the sharp rise of the curve occurs at the proper place corresponding to the neutralisation of two H^+ ions.

The dissociation constants k_1 and k_2 of the acid H_2X, where $X=[Re.(OH)_4.C_2O_4]^{2-}$ were calculated from the following deductions :

$$H_2X \rightleftarrows HX' + H^+; \quad \text{hence } k_1 = \frac{[HX'][H^+]}{[H_2X]} \qquad \ldots \quad (1)$$

$$HX' \rightleftarrows H^+ + X'' ; \text{ hence } k_2 = \frac{[H^+] \times [X'']}{[HX']} \quad \ldots \quad (2)$$

Let 'a' be the molar concentration of the total acid taken and titrated against a carbonate-free alkali of known strength, so that

$$a = a_2 + a_1 + a_0 \quad \ldots \quad \ldots \quad (3)$$

where a_2, a_1 and a_0 are the respective molar concentration of H_2X, HX' and X''; and let 'b' be the molar concentration of the alkali added. Then from a consideration of electrical neutrality of the solution, concentration of the positive ions may be equated with that of the negative ones, that is, of $b^+ + H^+$ with $X'' + HX' + OH'$

$$\text{or} \quad \underset{\text{(alkali consumed)}}{b^+ - OH'} = \underset{\text{(acid neutralised)}}{2a_0 + a_1 - H^+}.$$

$$b + H^+ - OH' = 2a_0 + a_1 \quad \ldots \quad \ldots \quad (4)$$

where $(b + H^+ - OH')$ is the amount of H^+ disengaged. Now, as the neutralisation takes place stepwise, it may be assumed that when,

$$(b + H^+ - OH') < a \; ; \; a_0 \text{ is negligibly small.}$$

$$\text{i.e., } a_0 \longrightarrow 0.$$

Therefore, from equations (3) and (4) we get,

$$a_1 = b + H^+ - OH',$$

$$a_2 = a - b - H^+ + OH'$$

$$k_1 = \frac{a_1 \times [H^+]}{a_2} = \frac{[b + H^+ - OH'] \times [H^+]}{[a - b - H^+ + OH']}$$

Again when $(b + H^+ - OH') > a$; $a_1 \longrightarrow 0$,

Then from the equations (3) and (4),

$$a_0 = b + H^+ - OH' - a$$

$$a_1 = 2a - b - H^+ + OH'$$

$$k_2 = \frac{a_0 \times [H^+]}{a_1} = \frac{[b + H^+ - OH' - a] \times [H^+]}{[2a - b - H^+ + OH']}$$

The average hydrogen ion bound to X'' at any time,

$$\bar{n} = \frac{2a_2 + a_1}{a}.$$

By plotting $\bar{n}$ against p_H, the values of k_1 and k_2 may be extrapolated from the corresponding values of p_H

$$\text{when } \bar{n} = 1.5, \qquad k_1 = [H^+]$$

$$\text{and when } \bar{n} = 0.5, \qquad k_2 = [H^+]$$

(Bjerrum, "Metal ammine formation in aqueous solutions", P. Hasse and Son, Copenhagen, 1941).

The values of k_1 and k_2 obtained for the rhenioxalic acid at 26° are respectively 7.94×10^{-3} and 1.02×10^{-5}.

It might be pointed out here that the value of k_1 may also be regarded as the dissociation constant of the monobasic form of the acid, *i.e.* of aquo-trihydroxo rhenioxalic acid. The first neutralisation is, however, never indicated by the curve under any condition, as the k_1 and k_2 values do not differ much. The acid is obviously stronger than acetic acid and is nearly as strong as oxalic acid.

In aqueous solution at low temperatures the acid occurs mainly in the monobasic or aquo-trihydroxo form. The freezing-point measurement shows that it dissociates mainly into two ions.

Under suitable conditions the various salts of the monobasic and of the dibasic acid have been prepared and their properties studied. The molar conductivity of the sodium salt at 25° of the monobasic acid and of the dibasic acid are 110 ohms^{-1} and 210 ohms^{-1} respectively, which are in good agreement with those for a uni-univalent and a uni-bivalent electrolyte.

The sodium salt of tetrahydroxo rhenioxalic acid has been found to be diamagnetic though it contains a tetrapositive rhenium. A tetrapositive rhenium should possess $75 - 4 = 71$ electrons around its nucleus, with 3 of these unpaired in the 5 *d* level. In an octahedral co-ordination with d^2sp^3 bonds, as in the present case, these three unpaired electrons in the 5 *d* level would remain undisturbed, giving rise to a paramagnetic moment of about 3.85 Bohr magnetons, on the basis of Bose-Stoner's rule. The diamagnetic character of the rhenioxalate complex therefore suggests the formation of metallic bonds between rhenium atoms in a dimeric ion of the complex, as shown below :

$$Na_4[C_2O_4.\ (OH)_4.\ Re \vdots \vdots Re.(OH)_4.\ C_2O_4].$$

The occurrence of a small temperature-independent paramagnetism in many simple rhenium compounds including ReO_2 examined by Schüth and Klemm (Z. *anorg. Chem.*, 1934, **220,** 193), as also in several rhenium complexes of ter- and pentavalent compounds (Klemm and Steinberg, *ibid.*, 1936, **227,** 193; Klemm and Frishmuth, *ibid.*, 1937, **230,** 220) furnishes a strong evidence in support of the tendency of the rhenium atom to form metallic bonds. The rhenioxalic acid complex has been derived from quadrivalent rhenium, and ReO_2 constitutes the starting material for its preparation. There is therefore every likelihood of the Re—Re metal bonding to occur in the rhenioxalic acid and its salts. The comparatively high value found by the cryoscopic method for the molecular weight of disodium tetrahydroxo rhenioxalate in solution seems to support this idea (*vide* experimental part).

EXPERIMENTAL

Scherring Kahlbaum's potassium perrhenate was used as the source of rhenium in all the preparations.

1. *Aquo-trihydroxo rhenioxalic Acid.*—Potassium rhenichloride was prepared from $KReO_4$, KI and concentrated HCl (Schmid, *loc. cit.*) and recrystallised from the same acid.

From potassium rhenichloride, black ReO_2 was obtained by treatment with an excess of caustic soda solution. The dioxide was filtered and washed thoroughly with distilled water, keeping it always under water to prevent oxidation.

ReO_2 (1 mol.) was refluxed in a round bottomed flask with an excess of oxalic acid (4 mols.) solution for about 2 to 3 hours, when all the ReO_2 dissolved giving a brown solution. The solution was then cooled, filtered and evaporated to dryness over sulphuric acid in vacuum. The dried product was then washed several times by decantation with pure dioxane (dried by refluxing with metallic sodium and distilling at 102°) to remove any excess of oxalic acid. It was then dried in a desiccator over concentrated sulphuric acid in vacuum.

The substance forms a black crystalline powder. It is highly soluble in water giving a deep brown solution. The solution reacts acidic. It is quite stable in acid medium but is readily decomposed by the addition of alkalies with the separation of ReO_2.

Rhenium was estimated as nitron perrhenate after removal as ReO_2, and oxalic acid in the filtrate by titration with permanganate solution after previous precipitation as calcium oxalate. {Found : Re, 48.83 ; C_2O_4, 23.12 ; H_2O (by loss at 110-115°), 9.43. $H[Re.(OH)_3.C_2O_4.H_2O]\ 2H_2O$ requires Re, 48.95 ; C_2O_4, 23.15 ; H_2O, 9.47 per cent}.

{Found (for the product dried at 110°-115°) : Re, 54.05 ; C_2O_4, 25.51. Calc. Re, 54.07 ; C_2O_4, 25.58 per cent}.

Cryoscopic measurement.

Wt. of the subs. taken (anhydrous, g./25 c.c.)	Δt.	M.W. (found).	M.W. (calc.).	vant Hoff's coeff.	Degree of dissociation.
0.2700	0.08°	251	344	1.37	0.37

About 37% of the substance dissociates at the melting point of ice. Hence the ionisation constant, k, is equal to 6.8×10^{-3}. This is in fair agreement with the pk_1 value determined below.

Potentiometric Titration of the Complex Acid by Alkali

A definite weight of the substance was dissolved in conductivity water in a Jena flask to make 0.01 *M* solution; 125 c.c. of this solution were taken in a Jena beaker provided with an electrically driven stirrer. A glass electrode and a calomel electrode were dipped into the acid solution and the p_H of the solution was measured by a Beckman p_H meter, model 6. From a burette, small quantities of a strong alkali of known strength were added drop by drop with constant stirring and the p_H of the resulting solution measured. The total volume of the alkali added was too small to effect any appreciable volume change. Results are recorded in Table I below, and represented in Fig. 1 and Fig. 2.

TABLE I

Alkali soln.=0.42*M*. $t = 26°$. Acid soln. = 0.01*M*.

Alkali added.	Molar conc. of alkali.	p_H on rapid titration.	p_H after waiting for equilibrium.	pk_1.	pk_2	$\bar{n}$.
0.0 c.c.	—	2.28	2.28	2.237	—	1.48
0.5	0.1674×10^{-2}	2.39	2.39	2.259	—	1.43
1.0	0.3348	2.57	2.57	2.367	—	1.40
1.5	0.5022	2.79	2.79	2.533	—	1.34
2.0	0.6696	3.18	3.18	2.735	—	1.26
2.5	0.8370	3.68	3.68	2.903	—	1.14
3.0	1.0044	4.45	3.90	—	6.367	1.00
3.5	1.1718	5.51	4.30	—	4.986	0.83
4.0	1.3392	8.30	4.60	—	4.891	0.66
4.5	1.5066	10.30	5.02	—	5.008	0.49
5.0	1.6740	10.73	5.49	—	5.274	0.32
5.5	1.8414	11.12	6.25	—	5.525	0.15
6.0	—	—	8.75	—	—	—
6.5			10.70	—	—	—

FIG. 1

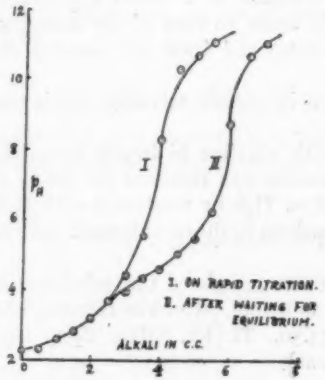
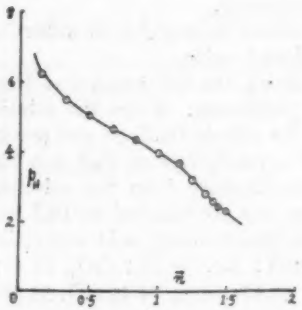


FIG. 2



From Fig. 2 $pk_1=2.10$ ($k_1=7.94\times10^{-3}$); $pk_2=4.99$ ($k_2=1.02\times10^{-5}$)

Salts of the Monobasic Form of the Acid

Sodium Aquo-trihydroxo rhenioxalate.—The sodium salt of the complex aquo-trihydroxo rhenioxalic acid was prepared by the addition of sodium acetate dissolved in aqueous alcohol to that of the acid in molecular proportion. The sodium salt of the complex acid was thereby precipitated. This was then filtered on the pump, washed 4 to 5 times with 70% alcohol and then thoroughly with absolute alcohol. Finally, it was dried in a desiccator over concentrated sulphuric acid.

The substance forms brownish black crystals, highly soluble in water but insoluble in organic solvents. Its solution reacts acidic (p_H 4). It is stable in acid solution, but is readily decomposed by alkalies.

For analysis, the substance was treated with ammonia and hydrogen peroxide to convert the rhenium to perrhenate. The mixture was then acidified with HCl (conc.) and rhenium removed as Re_2S_7. Sodium was then estimated as Na_2SO_4 in the filtrate. Rhenium was estimated as nitron perrhenate after the oxidation of Re_2S_7 with alkaline hydrogen peroxide. Oxalic acid was estimated in another sample of the substance by titration with permanganate after the removal of rhenium as ReO_2 by treatment with alkali as described before. {Found :

Re, 50.88 ; C_2O_4, 24.08; Na, 6.31. $Na[Re.(OH)_3.C_2O_4.H_2O]$ requires Re, 50.95; C_2O_4, 24.10 ; Na, 6.30 per cent}. The substance remains unchanged when dried at 110°-115°.

Equivalent conductance.

(t=25°)

v (litres)	256	512	1024
Δv	81.85	97.81	110.3

Molecular conductance=110.3 ohms^{-1} (approx.)

Potassium aquo-trihydroxo rhenioxalate was prepared by adding a solution of potassium acetate in alcohol to that of the complex acid in rectified spirit in equimolecular proportions. The potassium salt separated out from the solution. This was filtered, washed and dried as in the previous case.

The substance is insoluble in organic solvents, but highly soluble in water. {Found: Re, 48.74 ; C_2O_4, 23.10 ; K, 10.21. $K[Re.(OH)_3.C_2O_4.H_2O]$ requires Re, 48.81 ; C_2O_4, 23.10 ; K, 10.24 per cent}.

Thallium aquo-trihydroxo rhenioxalate was obtained as a brown crystalline precipitate by adding a solution of the thallous sulphate in water to that of the complex rhenioxalic acid. This was filtered, washed thoroughly with water and dried over concentrated sulphuric acid in a desiccator.

The substance is insoluble in water as well as in organic solvents, but is readily soluble in dilute mineral acids.

For analysis, the substance was treated with alkaline hydrogen peroxide to convert rhenium to perrhenate. From the solution rhenium was removed as Re_2S_7 as described before. In the filtrate thallium was precipitated as Tl_2S by treatment with H_2S in alkaline medium. The precipitate of Tl_2S was then dissolved in dilute sulphuric acid and thallium estimated as chromate from the solution.

Thallium was precipitated as TlCl from another sample of the substance by means of HCl. In the filtrate oxalic acid was estimated as before, after the removal of rhemium as ReO_2. {Found : Re, 30.45 ; C_2O_4, 14.46; Tl, 33.50. Tl [Re. $(OH)_3$. C_2O_4. H_2O], 3.5 H_2O requires Re, 30.54 ; C_2O_4, 14.45 ; Tl, 33.50 per cent}.

Barium aquo-trihydroxo rhenioxalate was prepared by double decomposition between barium chloride and the sodium aquo-trihydroxo rhenioxalate in aqueous solution. The precipitated barium salt was washed thoroughly with water and then with a little alcohol. This was then dried in a desiccator over concentrated sulphuric acid.

The substance forms deep brown crystals insoluble in water and organic solvents, but readily soluble in meneral acids.

Barium was estimated as $BaSO_4$ from an acid solution of the substance. From the filtrate Re and oxalic acid were estimated as already described. {Found : Re, 40.82; C_2O_4, 19.27 ; Ba, 15.08. $Ba[Re.(OH)_3.C_2O_4.H_2O]$, $5H_2O$ requires Re, 40.83 ; C_2O_4, 19.32 ; Ba, 15.04 per cent}.

Lead aquo-trihydroxo rhenioxalate.—A solution of lead acetate in water was added drop by drop to an aqueous solution of the sodium aquo-trihydroxo rhenioxalate. The lead salt separated out in the form of a grey crystalline powder. This was washed and dried as usual.

The lead salt is insoluble in water, but dissolves in dilute mineral acids.

Lead was estimated as $PbSO_4$ by digestion of the substance with dilute H_2SO_4. Re and oxalic acid were estimated in the filtrate as usual. {Found : Re, 41.72 ; C_2O_4, 19.72 ; Pb, 23.20. Pb [Re. $(OH)_3$. C_2O_4. H_2O] requires Re, 41.75 ; C_2O_4, 19.77; Pb, 23.23 per cent}.

Salts of the Dibasic Form of the Acid

Sodium tetrahydroxo rhenioxalate was prepared by the addition of an excess of sodium acetate to the aquo-trihydroxo complex acid in aqueous alcoholic solution. The sodium salt, which separated out, was filtered on the pump. This was dissolved in a little water and reprecipitated by the addition of sodium acetate solution in rectified spirit. It was then filtered, washed 4 to 5 times with 70% alcohol and then thoroughly with absolute alcohol. Finally, the product was dried in a desiccator over concentrated sulphuric acid.

The substance forms a grey crystalline powder, highly soluble in water but insoluble in organic solvents. The solution reacts almost neutral to litmus. It is stable in acid solution, but readily decomposes in alkali. {Found : Re, 43.82 ; C_2O_4, 20.71 ; Na, 10.85. $Na_2[Re.(OH)_4.C_2O_4]2H_2O$ requires Re, 43.86; C_2O_4 , 20.76 ; Na, 10.85 per cent}.

The two molecules of water could not be removed by drying even at 110°-115°.

Magnetic susceptibility.—The susceptibility was measured in a Gouy's balance $\chi_g = -0.00938 \times 10^{-6}$; $\chi_M = -3.98 \times 10^{-6}$.

Cryoscopic measurements. —The molecular weight of the disodium salt was determined by lowering of the freezing-point method.

Substance (on anhydrous basis, g./25 c.c.)	Depression Δt.	M. W. (found).	M. W. (calc.).	vant Hoff's coeff.	Degree of dissociation.
0.0915	0.04°	164.7	388	2.36	0.68

The result shows that only about 68% of the salt appears to dissociate at the melting point of ice. This abnormally low value suggests its dimeric character.

Equivalent conductance measurement.

$t = 25°$.

v (litres)	16	32	64	128	256	512	1024
Δ_v	51.90	52.65	67.10	72.10	79.60	89.0	105.15

Molecular conductance = 210.3 $ohms^{-1}$ (approx.).

Potassium tetrahydroxo rhenioxalate was prepared by the action of an alcoholic solution of potassium acetate on that of the complex rhenioxalic acid in water. The compound precipitated out completely by the addition of a further amount of alcohol. It was filtered, dissolved in water and reprecipitated by the addition of alcohol. This was again filtered, dissolved in water and reprecipitated by the addition of a concentrated solution of potassium acetate in alcohol. The precipitate was washed thoroughly with rectified spirit and then with absolute alcohol and finally dried in a desiccator over sulphuric acid.

The substance forms dark brown crystals, highly soluble in water, but insoluble in organic solvents. {Found : Re, 37.62 ; C_2O_4, 17.84 ; K, 15.82. $K_2[Re.(OH)_4.C_2O_4].4H_2O$ requires Re, 37.80 ; C_2O_4, 17.89 ; K, 15.85 per cent}.

Ammonium tetrahydroxo rhenioxalate was prepared exactly like the potassium salt using ammonium acetate in place of potassium acetate. The substance forms a brown powder, highly soluble in water, but insoluble in organic solvents. {Found : Re, 42.02 ; C_2O_4, 19.93; NH_4, 8.23. $(NH_4)_2[Re.(OH)_4.C_2O_4]$, $3.5H_2O$ requires Re, 42.18 ; C_2O_4, 19.95 ; NH_4, 8.16 per cent}.

Lithium tetrahydroxo rhenioxalate was prepared by the action of lithium carbonate on the acid. An alcoholic solution of lithium carbonate was added drop by drop with constant stirring to an aqueous solution of the complex aquo-trihydroxo rhenioxalic acid. The mixture was allowed to stand for 15 minutes and the lithium salt was then precipitated by the addition of a further quantity of alcohol. This was filtered, dissolved in the minimum quantity of water and again reprecipitated by the addition of a concentrated solution of lithium carbonate in alcohol. The product was washed free from Li_2CO_3 with alcohol and then dried in a desiccator over sulphuric acid.

The substance forms deep brown crystals, soluble in water and also to some extent in aqueous alcohol, but insoluble in absolute alcohol and dioxane.

This was analysed like the corresponding sodium or potassium salt and lithium was estimated as Li_2SO_4. {Found : Re, 40.05; C_2O_4, 18.93; Li, 2.97 ; Li [Re. $(OH)_4.C_2O_4$], $6H_2O$ requires Re, 40.09 ; C_2O_4, 18.96 ; Li, 2.99 per cent}.

Barium tetrahydroxo rhenioxalate was obtained as a brown precipitate by the addition of an aqueous solution of barium chloride to that of the corresponding sodium salt. This was filtered, washed and dried as usual.

The substance forms brown crystals insoluble in water, but soluble in dilute mineral acids. {Found : Re, 38.73 ; C_2O_4, 18.32 ; Ba, 28.62. Ba [Re. $(OH)_4.C_2O_4$] requires Re, 38.83 ; C_2O_4, 18.37 ; Ba, 28.92 per cent}.

Calcium tetrahydroxo rhenioxalate was prepared by the addition of calcium chloride solution to that of the disodium tetrahydroxo rhenioxalate. The precipitated calcium salt was washed and dried as in the previous cases. It resembles the barium salt in its properties.

For analysis, rhenium was first removed as Re_2S_7 in the manner described for the analysis of the thallium salt of the monobasic acid. In the filtrate from Re_2S_7, calcium was precipitated as calcium oxalate and estimated volumetrically. Rhenium was estimated from the precipitated Re_2S_7 as nitron perrhenate.

From another sample, rhenium was precipitated as ReO_2 by alkalies. The mixture was then acidified to dissolve any precipitate of calcium oxalate. In the filtrate from ReO_2, oxalic acid was estimated volumetrically after precipitation as calcium oxalate. {Found : Re, 48.46 ; C_2O_4, 23.02 ; Ca, 10.47. Ca [Re. $(OH)_4.C_2O_4$] requires Re, 48.69; C_2O_4, 23.03 ; Ca, 10.47 per cent}.

Strontium tetrahydroxo rhenioxalate was prepared by double decomposition between strontium chloride and the disodium rhenioxalate as in the case of the calcium salt.

Strontium was estimated as $SrSO_4$ after the precipitation of Re as Re_2S_7.

Oxalic acid was estimated in another sample as described in the case of the calcium salt above. [Found : Re, 43.29; C_2O_4, 20.48 ; Sr, 20.39. Sr [Re. $(OH)_4.C_2O_4$] requires Re, 43.30; C_2O_4, 20.48; Sr, 20.39 per cent}.

Lead Tetrahydroxo rhenioxalate.—When a solution of lead acetate in water was added dropwise to an aqueous solution of the complex sodium salt, the insoluble lead salt separated out in the form of a grey crystalline powder. This was washed and dried as usual. {Found : Re, 33.87 ; C_2O_4, 16.01; Pb, 37.74. Pb [Re. $(OH)_4$. C_2O_4] requires Re, 33.88; C_2O_4, 16.03; Pb, 37.70 per cent}.

Copper Tetrahydroxo rhenioxalate.—A solution of copper acetate in rectified spirit was added to an aqueous solution of the complex acid. The mixture was allowed to stand for a while when a grey precipitate settled down. This was filtered, washed and dried as usual.

The substance is slightly soluble in water, but insoluble in organic solvents. When decomposed with alkali, the substance gives first a yellow precipitate and on heating on the

water-bath the yellow precipitate turns chocolate-brown. Cupric ion in solution was therefore reduced to the cuprous state by the quadrivalent rhenium and the cuprous tetrahydroxo rhenioxalate was precipitated.

For analysis, the substance was treated with alkaline hydrogen peroxide. The precipitated copper oxide was filtered and estimated iodometrically. Rhenium was estimated in the filtrate as usual.

Oxalic acid was estimated as in the case of calcium or strontium salt after the removal of rhenium as ReO_2. {Found : Re, 38.91 ; C_2O_4, 18.41 ; Cu 26.57. Cu_2[Re. $(OH)_4.C_2O_4$], $0.5H_2O$ requires Re, 38.91; C_2O_4, 18.41 ; Cu, 26.57 per cent}.

Zinc tetrahydroxo rhenioxalate.—Zinc acetate was dissolved in rectified spirit and was added to the aqueous solution of the complex acid, when the zinc salt of the acid separated out. This was washed thoroughly first with dilute alcohol and then with absolute alcohol and finally dried as before.

The substance forms a grey crystalline powder, slightly soluble in water, and insoluble in organic solvents.

Zinc was estimated as zinc ammonium phosphate after the removal of rhenium as Re_2S_7, as described before.

Oxalic acid was also estimated in the manner described for the calcium salt. {Found: Re, 40.37 ; C_2O_4, 19.09 ; Zn, 14.17. Zn[Re. $(OH)_4$ .C_2O_4], $3H_2O$ requires Re, 40.31 ; C_2O_4, 19.07 ; Zn, 14.17 per cent}.

Cadmium tetrahydroxo rhenioxalate was prepared by adding a solution of cadmium acetate in rectified spirit to an aqueous solution of the complex aquo-trihydroxo rhenioxalic acid. The precipitated cadmium salt was filtered and again digested with cadmium acetate solution in rectified spirit. The product was washed and dried as usual. It resembles the zinc salt in properties.

Cadmium was estimated as cadmium oxinate after the removal of rhenium as Re_2S_7.

Rhenium and oxalic acid were estimated as in the case of the zinc or calcium salt. [Found : Re, 39.31 ; C_2O_4, 18.57 ; Cd, 23.82. Cd [Re. $(OH)_4.C_2O_4$], H_2O requires Re, 39.37 ; C_2O_4, 18.65 ; Cd, 23.79 per cent}.

Nickel tetrahydroxo rhenioxalate.—Nickel acetate was dissolved in rectified spirit and was added drop by drop to an aqueous solution of the aquo-trihydroxo rhenioxalic acid with stirring. The mixture was allowed to stand for a while when the nickel salt separated out in the form of a grey crystalline powder. This was washed and dried as usual.

The process of analysis resembled that of the zinc or cadmium salt, nickel being estimated as nickel dimethylglyoxime. {Found : Re, 42,59; C_2O_4, 20.16; Ni, 13.49. Ni [Re. $(OH)_4$.-C_2O_4], $2H_2O$ requires Re, 42·59 ; C_2O_4, 20.15; Ni, 13.48 per cent}.

Cobalt tetrahydroxo rhenioxalate was prepared by the action of cobalt acetate on the complex acid as described in the case of the nickel salt.

The substance forms a deep brown crystalline powder, soluble in water, but insoluble in organic solvents.

The method of analysis was similar to that employed for the nickel salt, cobalt being estimated as $CoSO_4$. {Found : Re, 44.35; C_2O_4, 20.93 ; Co, 14.05. Co [Re. $(OH]_4.C_2O_4$], H_2O requires Re, 44.40 ; C_2O_4, 21.00 ; Co, 14.06 per cent}.

Hexamine tetrahydroxo rhenioxalate was prepared by adding an excess of hexamethylenetetramine solution in alcohol to an alcoholic solution of the complex aquo-trihydroxo rhenioxalic acid. The substance separated out in the form of a black crystalline powder. The product was redissolved in a little water, filtered to separate any ReO_2 formed, and repre-

cipitated by the addition of alcohol. This was washed and dried as usual. The substance is highly soluble in water, but insoluble in organic solvents. Nitrogen was estimated by Kjeldahl's process. {Found : Re, 35.76 ; C_2O_4, 16.96 ; N, 10.75. $(CH_2)_6N_4$, $H_2[Re.(OH)_4.C_2O_4]$, $2H_2O$ requires Re, 35.78 ; C_2O_4, 16.92 ; N_2, 10.78 per cent}.

Strychnine tetrahydroxo rhenioxalate.—Strychnine acetate was dissolved in alcohol and was added drop by drop with constant stirring to an alcoholic solution of the complex acid. The strychnine salt separating was redissolved in a little water and reprecipitated by the addition of an alcoholic solution of strychnine acetate, washed and dried as usual. The substance forms a dark grey crystalline powder, insoluble in organic solvents, but soluble in water.

Rhenium was estimated as nitron perrhenate after removal as Re_2S_7 in the manner described before. Nitrogen was estimated by Duma's method. {Found : Re, 16.58; C, 47.06 ; N, 5.00. $(C_{21}H_{22}O_2N_2)_2$, $H_2[Re.(OH)_4.C_2O_4]$, $6H_2O$ requires Re, 16.61 ; C, 47.14 ; N, 5.00 per cent}.

With silver salt solutions rhenioxalic acid and its salts are oxidised to give perrhenic acid or perrhenates, and silver is reduced to the metallic state.

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STUDIES ON THE CHEMISTRY OF RHENIUM. PART II. COMPLEX COMPOUNDS OF QUADRIVALENT RHENIUM WITH GALLIC ACID

By Debabrata Sen and Priyadaranjan Rây

Like oxalic acid (cf. Part I) gallic acid has also been found to combine with quadrivalent rhenium to give rise to a complex acid, which has the composition $H_2[(H_2O)_2.\ Re(C_6H_2O_2.OH.COO)_2].6H_2O$. The dissociation constants, k_1 and k_2 of the acid, as determined by potentiometric titration, are given by the values 7.1×10^{-5} and 4.4×10^{-7} respectively. A number of alkali, alkaline earth and heavy metal salts of the acid have been described. The sodium salt of the acid like the corresponding rhenioxalate has been found to be diamagnetic.

The complex compounds of quadrivalent rhenium with oxalic acid have been described in the previous paper (this *issue* p. 171). A complex acid of similar type has now been prepared by the action of gallic acid on pure recrystallised potassium rhenichloride. Its composition may be represented by the formula $H_2[Re.(H_2O)_2.(C_6H_2O_2.\ OH.COO)_2].\ 6H_2O$. Of the six water molecules four can easily be removed at 110° – 115°. The alkali salts, even when dried at 110° – 115°, have the composition represented by $M_2\ [Re\ (H_2O)_2.\ (C_6H_2O_2.OH.COO)_2]$.

Molecular conductance at infinite dilution of the sodium salt was found to be about 220 ohms^{-1}. This is in agreement with the molar conductance of the uni-bivalent electrolyte.

A series of salts, such as those of sodium, potassium, barium, calcium, lead, thallium, etc., was prepared and studied. The alkali salts are soluble in water, but those of alkaline earth, lead and thallium are insoluble.

Potentiometric titration of the acid with alkali shows that the acid is a dibasic one. The dissociation constants k_1 and k_2 of the acid are 7.1×10^{-5} and 4.4×10^{-7} respectively (cf. Part I, *loc. cit.*). The first inflexion of the curve was not obtained, as the values of k_1 and k_2 do not differ much. The complex rhenigallic acid appears to be as strong as the gallic acid itself. ($k=4.8\times10^{-5}$; Ostwald, *Z. physikal. Chem.*, 1889, **3**, 252).

Like the rhenioxalate complexes, sodium rhenigallate has also been found to show a diamagnetic susceptibility, indicating the presence of metallic bonds between rhenium atoms in a dimeric formula.

Experimental

Diaquo-rhenigallic Acid.—Crude potassium rhenichloride was recrystallised from concentrated hydrochloric acid. The pure product (1 *M*) was mixed with gallic acid (4 *M*, Merck's reagent) in a little water. The mixture was refluxed in a small R.B. flask for about an hour, when a dark brown solution was obtained. This was cooled, filtered and evaporated to dryness in a vacuum desiccator over concentrated sulphuric acid. The residue was extracted with absolute alcohol to remove potassium chloride. This was filtered and the alcoholic solution again evaporated to dryness in a vacuum desiccator over concentrated sulphuric acid.

The substance forms deep brown crystals, which reacts acidic in solution. It is highly soluble in water and alcohol ; but once dried, it goes very slowly into solution. The substance is quite stable in acid medium, but slowly oxidises in the presence of alkalies.

For analysis, the substance was decomposed with alkali and hydrogen peroxide. From the solution rhenium was estimated as nitron perrhenate.

Carbon and hydrogen were estimated in a semi-micro combustion system.

{Found : Re, 27.94 ; C, 25.19 ; H, 3.58 ; H_2O (by dehydration at 110°-115°), 11.03. $H_2[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$, $6H_2O$ requires Re, 27.93 ; C, 25.22 ; H, 3.60 ; H_2O, 16.22 per cent}.

Thus only a part of the water was removed by drying at 110°-115°. {Found (for the product dried at 110-115°): Re, 31.30; C, 28.31 ; H, 2.66. H_2 [Re. $(H_2O)_2$. $(C_6H_2O_2.OH.COO)_2$], $2H_2O$ requires Re, 31.31 ; C, 28.28 ; H, 2.70 per cent}.

Potentiometric titration of the acid.—The acid was titrated against alkali potentiometrically. (cf. Figs. 1 and 2)

TABLE I

Alkali soln.$=0.4645M$. Acid soln.$=0.0075M$. $t=25°$.

Alkali added.	Molar conc. of alkali.	p_H	k_1.	k_2.	$\bar{n}$.
0 c.c.	—	2.88	3.550	—	1.82
0.4	0.1858×10^{-2}	3.65	4.065	—	1.72
0.8	0.3716	4.15	4.135	—	1.49
1.2	0.5574	4.63	4.162	—	1.25
1.6	0.7432	5.16	3.074	—	1.61
2.0	0.9290	5.72	—	6.224	0.76
2.4	1.1148	6.32	—	6.344	0.52
2.8	1.3524	7.30	—	6.689	0.20
3.2	1.4864	8.58	—	6.846	0.018
4.0	—	10.25	—	—	—

FIG. 1

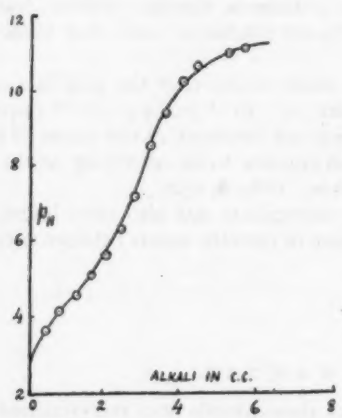
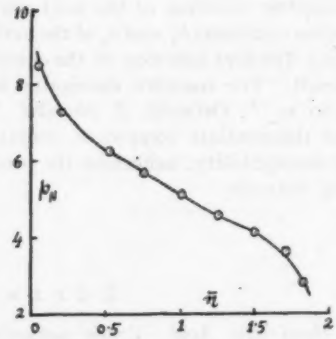


FIG. 2



From Fig. 2 $pk_1 = 4.15$; $k_1 = 7.1\times10^{-5}$
$pk_2 = 6.36$; $k_2 = 4.4\times10^{-7}$

Sodium Salt of the Diaquo-rhenigallic Acid.—A concentrated solution of sodium acetate in rectified spirit was added with constant stirring to an alcoholic solution of the complex acid. The sodium salt separating was allowed to stand for a while with frequent shaking. This was filtered and treated with a concentrated solution of sodium acetate in alcohol. The product was then filtered, washed thoroughly at first with rectified spirit and then with alcohol. Finally, it was dried in a desiccator over concentrated sulphuric acid.

The substance forms a light brown crystalline powder. It is highly soluble in water, but insoluble in organic solvents. The substance is quite stable in acid, but is rapidly oxidised in presence of alkali. Its aqueous solution reacts alkaline. {Found : Re, 30.90 ; C, 27.92;

H, 1.62 ; Na, 7.64. $Na_2[(Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$ requires Re, 30.90 ; C, 27.91 ; H, 1.66 ; Na, 7.64 per cent}.

On drying at 110°-115° the substance remained unchanged.

For analysis, the substance was decomposed with ammoniacal hydrogen peroxide and rhenium was separated as Re_2S_7. In the filtrate sodium was estimated as Na_2SO_4. Rhenium was estimated as nitron perrhenate after oxidation of the sulphide to perrhenate.

Magnetic susceptibility was measured in a Gouy's balance. $\chi_g = -0.00863 \times 10^{-6}$; $\chi_M = -4.391 \times 10^{-6}$.

Equivalent conductance.

$t = 25°$.

Dilution (litres) ..	32	64	128	256	512	1024
Λ_v ..	58.2	72.9	79.5	87.3	98.2	109.9

Mol. conductance = 220 ohms^{-1} approx.

Potassium Salt.—An alcoholic solution of potassium acetate was added dropwise to a similar solution of rhenigallic acid. The potassium salt separating as a brown powder was filtered and again digested with an alcoholic solution of potassium acetate. The mixture was allowed to stand for a while and then filtered. The product was washed and dried as usual. The substance is highly soluble in water, but insoluble in organic solvents.

Potassium was estimated as potassium sulphate after removal of rhenium as in the previous case. {Found : Re, 29.32 ; C, 26.44 ; H, 1.59 ; K, 12.26. $K_2[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$ requires Re, 29.33 ; C, 26.50 ; H, 1.58 K, 12.30 ; per cent}.

Ammonium salt was prepared exactly in the same manner as the potassium salt. The substance forms a brown crystalline powder and resembles the alkali salts in properties. Ammonia was estimated by Kjeldahls' method. {Found : Re, 31.30 ; NH_4, 6.08. $(NH_4)_2[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$ requires Re, 31.31 ; NH_4, 6.06 per cent}.

Thallium Salt.—An aqueous solution of the thallous sulphate was added dropwise to that of the sodium salt of the rhenigallic acid. The insoluble thallium salt separating as a brown precipitate was washed and dried as usual.

The substance is insoluble in water and organic solvents, but soluble in dilute mineral acids.

For analysis, the substance was decomposed with alkaline hydrogen peroxide and from the acidified solution rhenium was precipitated as Re_2S_7. From the filtrate thallium was precipitated as Tl_2S in alkaline medium. This was dissolved and estimated as thallous chromate. {Found : Re, 19.25 ; Tl, 42.22. $Tl_2[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$ requires Re, 19.29 ; Tl, 42.32 per cent}.

Barium Salt.—A solution of barium chloride was added drop by drop to that of the sodium salt of the complex acid. The barium salt that separated out, was washed and dried as in the other cases. The substance is insoluble in water and organic solvents, but readily soluble in dilute mineral acids.

For analysis, the substance was trreated with alkaline hydrogen peroxide and from the acidified solution barium was precipitated and estimated as $BaSO_4$. From the filtrate rhenium was precipitated as Re_2S_7 and then oxidised and estimated as usual. {Found : Re, 24.33; Ba, 17.87. $Ba[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$ requires Re, 24.32; Ba, 17.91 per cent}.

Calcium Salt.—This was prepared from an aqueous solution of calcium chloride and that of the sodium salt of the complex acid. The brown precipitate of the calcium salt was washed and dried as in the previous cases.

The substance was decomposed with ammoniacal hydrogen peroxide; and from the acidified solution rhenium was separated as Re_2S_7. From the filtrate calcium was estimated as $CaSO_4$ after evaporation and heating with sulphuric acid. {Found: Re, 29.41; Ca, 6.30. $Ca[Re.(H_2O)_2(C_6H_2O_2)OH.COO)_2]$, $2H_2O$ requires Re, 29.43; Ca, 6.33 per cent.}

Lead salt was obtained as a brown crystalline precipitate from an aqueous solution of the lead acetate and that of the sodium salt of the complex acid. The product was washed and dried as in all other cases.

Lead was estimated as lead sulphate following the procedure described under barium salt. {Found : Re, 23.51 ; Pb, 26.16. Pb $[Re.(H_2O)_2.(C_6H_2O_2.OH.COO)_2]$, 1.5 H_2O requires Re, 23.54 ; Pb, 26.20 per cent}.

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A STUDY OF THE COMPLEX COMPOUNDS OF DIGLYCYLETHYLENEDIAMINE WITH BIVALENT METALS

By Amiya Kumar Chakraburtty, Nripendra Nath Ghosh and Priyadaranjan Rây

Diglycylethylenediamine, ($—CH_2 NH. CO. CH_2NH_2)_2$, has been found to form complexes with bivalent metals like copper, nickel, zinc, cadmium and magnesium, acting as a quadridentate ligand by furnishing four points of attachment from its four nitrogen atoms.

The determination of the two acid dissociation constants (k^*_1 and k^*_2) of the ligand base and a quantitative study of the mechanism of formation and decomposition of the complexes of diglycylethylenediamine with the five bivalent metal ions, viz. Cu^{++} Ni^{++}, Zn^{++}, Cd^{++} and Mg^{++}, have been made by the physicochemical method developed by Bjerrum.

The stability of the corresponding complexes were found to follow the order Cu > Ni > Zn > Cd > Mg, having the pK values 8.13, 5.42, 4.31, 3.33, and 0.54, respectively.

In the case of copper and nickel the stepwise hydrolysis of the complex cations was studied and the two hydrolysis constants K_{h_1} and K_{h_2} determined. The electrolytic dissociation constants, $k^*_{b_1}$ and $k^*_{b_2}$, of the corresponding complex bases were also derived therefrom.

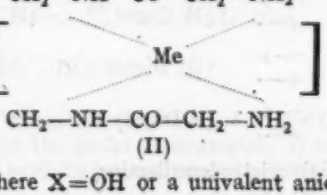
The complex copper and nickel bases and their chlorides have been isolated in a pure state and their properties studied. The colour of the bases and of the salts differ widely suggesting a difference in the nature of the complex cations in the two cases. The complex bases probably belong to the penetration type with planar hybrid dsp^2 bonds, whereas the salts are characterised mostly by ionic or ion-dipole co-ordination bonds. This has been supported by the measurement of magnetic moments of the compounds.

Pfeiffer and Saure (*J. prakt. Chem.*, 1941, **157**, 116) in a comprehensive study of the mechanism of biuret reaction and of the structure of the resulting compounds have described the preparation and properties of a large number of co-ordination complexes formed by various organic reagents, similar in character to biuret; as for example, glycylamide, glycylanilide, glycylglycine, diglycylethylenediamine, etc., with metals of the first transitional series (Cu and Ni). Of these, diglycylethylenediamine (I), which is assumed to serve as a quadridentate ligand, was first prepared by them in the form of hygroscopic needles. This was found by them to give a deep violet solution with copper acetate or copper hydroxide and alkali, but the resulting complex could not be isolated in a pure crystalline condition.

$$\begin{array}{l} CH_2 — NH — CO — CH_2 — NH_2 \\ | \\ CH_2 — NH — CO — CH_2 — NH_2 \end{array}$$

(I)

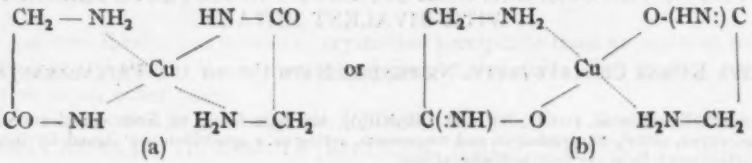
In continuation of the work on the study of the complex compounds of biguanide, dicyandiamidine and thiodicyandiamidine (guanylthiourea), which had been carried out in this laboratory for several years, it was considered of interest to investigate the formation, stability and the preparation in pure crystalline state of the complex compounds of diglycylethylenediamine with bivalent metals like copper, nickel, zinc, cadmium, etc. As a result, we have succeeded in preparing the copper and nickel complexes of the ligand, in the form of both as free bases as well as their salts. These have been found to possess a structure (II) as shown below.



(II)

(where X=OH or a univalent anion).

This structure, however, differs from that suggested by Pfeiffer and Saure (*loc. cit.*) for complexes with ligands of this type. Taking, for instance, the case of glycylamide, they have discussed about two possible structures of the inner-metallic type (a) and (b) for its copper complex, as represented below:



But they further pointed out that as diglycyl*ortho*phenylenediamine, in which the two amido-N atoms are linked by a short bridge, gave a violet-coloured copper compound, preference should be given to the structure (a).

The copper and nickel complexes of diglycylethylenediamine prepared by us are highly soluble in water and show distinctly different colours in alkaline and neutral solutions. They have been isolated both as free base as well as salts, showing that they are not inner-metallic complex of the type described by Pfeiffer and Saure (*loc. cit.*). The complex copper base forms red-violet crystals which give a deep permanganate-red solution in water; while the salt (chloride) of the complex base forms deep blue flakes. The complex nickel base gives rise to a bright yellow hygroscopic powder which forms a deep yellow solution in water. The yellow base is diamagnetic. But the salt (chloride) of the yellow base is bluish green and has been found to be paramagnetic, giving a moment value of $2.8\mu_B$, identical with that for a simple nickel ion. This seems to suggest a difference in the type of the co-ordination bonds in the base and the salt. The diamagnetic base consequently possesses a planar structure with strong dsp^2 hybrid bonds giving rise to a penetration complex, while the salt may be represented as an ionic complex with ion-dipole bonds or as an associated complex with weak sp^2d hybrid bonds, resonating with the ionic type. The same distinction may be assumed to hold good in the case of the complex copper base (red-violet) and its chloride (blue), as suggested by their respective magnetic moments of 1.7 and $1.92\mu_B$ (cf. Rây and Sen, this *Journal*, 1948, **25**, 473). Thus, the high solubility of these complexes in water with formation of their characteristic cations and their magnetic properties furnish definite evidences against their structure as inner-metallic compounds as suggested by Pfeiffer and Saure (*loc. cit.*).

In order to gain further insight into the behaviour of these compounds, the formation and stability of the diglycylethylenediamine complexes of the bivalent metals, zinc, cadmium and magnesium, besides copper and nickel, were studied, following the physico-chemical method of Bjerrum ("Metalammine Formation in Solution", P. Haase and Son, Copenhagen, 1941). The stability of the copper and nickel complexes were also studied from the decomposition of the respective complex bases, taking advantage of their availability in the free solid state.

The reaction between diglycylethylenediamine dihydrochloride, [Diged H_2] Cl_2, and a bivalent metal ion M^{++}, may be assumed to take place in successive stages with the gradual addition of alkali, as represented below:

$$M^{++} + \text{Diged } H_2^{++} \rightleftharpoons [\text{M Diged}]^{++} + 2H^+ \quad .. \quad (1)$$

$$[\text{M Diged}]^{++} + H_2O \rightleftharpoons [(\text{M Diged})(OH)]^+ + H^+ \quad .. \quad (2)$$

$$[(\text{M Diged})(OH)]^+ + H_2O \rightleftharpoons [\text{M Diged}](OH)_2 + H^+ \quad .. \quad (3)$$

(where Diged = 1 molecule of diglycylethylenediamine).

The respective equilibrium constants K'_f, K_{h_1} and K_{h_2} may be determined from the relations given below :

$$K'_f = \frac{[\text{M Diged}^{++}] \times [\text{H}^+]^2}{[\text{M}^{++}] \times [\text{Diged H}_2^{++}]} \quad .. \quad .. \quad (4)$$

$$K_{h_1} = \frac{[\{(\text{M Diged})(\text{OH})\}^+] \times [\text{H}^+]}{[\text{M Diged}^{++}]} \quad .. \quad .. \quad (5)$$

$$\text{and } K_{h_2} = \frac{[(\text{M Diged})(\text{OH})_2] \times [\text{H}^+]}{[\{(\text{M Diged})(\text{OH})\}^+]} \quad .. \quad .. \quad (6)$$

by measuring the p_H values of the reacting mixture during titration with a standard solution of carbonate-free alkali and knowing the acid dissociation constant values, k^*_2 and k^*_1, of the ligand DigedH_2^{++} from the consideration of the following equations :

$$\text{DigedH}_2^{++} \rightleftarrows \text{DigedH}^+ + \text{H}^+ \quad .. \quad (7)$$

$$\text{DigedH}^+ \rightleftarrows \text{Diged} + \text{H}^+ \quad .. \quad (8)$$

From these k^*_2 and k^*_1 can be derived as

$$k^*_2 = \frac{[\text{Diged H}^+].[\text{H}^+]}{[\text{Diged H}_2^{++}]} \quad .. \quad .. \quad (9)$$

$$k^*_1 = \frac{[\text{Diged}].[\text{H}^+]}{[\text{Diged H}^+]} \quad .. \quad .. \quad (10)$$

The values of these constants, ((k^*_2 and k^*_1), were determined by measuring the p_H values of the solution resulting from the progressive addition of alkali to the dihydrochloride of the base as described by De, Ghosh and Rây (this *Journal*, 1950, **27**, 493) for biguanide and substituted biguanides (cf. also Carlson, McReynolds and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334).

While treating gradually a mixture of the metal ion and an excess of $(\text{Diged H}_2)^{++}$ in presence of some free acid with an alkali solution, if C denote the molar concentration of the total MCl_2 taken and C_o, C_d, C_{h_1} and C_{h_2}, the respective molar concentrations of M^{++}, $[\text{M Diged}]^{++}$, $[(\text{MDiged})(\text{OH})]^+$ and $[(\text{M Diged})(\text{OH})_2]$ present at any time, then

$$C = C_o + C_d + C_{h_1} + C_{h_2} \quad .. \quad (11)$$

and if X denote the total diamine as dihydrochloride, then

$$X = B_o + B_1 + B_2 + C_d + C_{h_1} + C_{h_2} \quad .. \quad (12)$$

where B_O, B_1 and B_2 are the molar concentrations of Diged, $(\text{Diged H})^+$ and $(\text{Diged H}_2)^{++}$ respectively. Further let P be the molar concentration of the added alkali (KOH) and A, the molar concentration of the initially present free acid in the reacting mixture at any time.

Now, as the solution is electrically neutral, the cationic and the anionic charges in it must be equal. Therefore,

$$2\,M^{++} + 2\,[M\,Diged]^{++} + [(M\,Diged)\,(OH)]^{+} + K^{+} + H^{+} + [Diged\,H]^{+}$$

$$+2\,[Diged\,H_2]^{++} = Cl^{-} + OH^{-} \quad .. \quad (13)$$

$$i.e.\ 2C_o+2C_d+C_{h_1}+P+[H^+]+B_1+2B_2 = 2C+2X+A+OH^- \quad .. \quad (14)$$

Then, as the reactions (1), (2) and (3) take place with the release of acid (H^+ ion), there may arise three cases as shown below :

Case I. When the total acid disengaged is less than $2C$, the formation of $[(MDiged)(OH)]^+$ (vide eqn. (2)] and $[(MDiged)(OH)_2]$ [eqn. (3)] may be regarded as negligible. From (11), (12), (14), (9) and (10) assuming C_{h_1} and $C_{h_2}=0$, we get

$$B_2=\frac{[H^+]}{k^*_2+2[H^+]}\times(2X-P+A-[H^+]+[OH^-]) \quad .. \quad (15)$$

$$C_d=1/2\,(P+[H^+]\,-A-[OH^-]) - \frac{[H^+]\,k^*_2+2k^*_1\,k^*_2}{2[H^+]\,k^*_2+4[H^+]^2}\,(2X-P+A-[H^+]+[OH^-]) \quad (16)$$

$$C_o=1/2\,(2C-P+A-[H^+]+[OH^-]) + \frac{[H^+]k^*_2+k^*_1\,k^*_2}{2[H^+]k^*_2+4[H^+]^2} = (2X-P+A-[H^+]+[OH^-] \quad ..(17)$$

From these,

$$K'_f = \frac{C_d\times[H^+]^2}{C_o\times B_2} \quad .. \quad .. \quad (18)$$

The value of K'_f, can also be obtained by plotting $\bar{n}_d$, the average ligandamine bound to metal atoms (given by C_d/C) against $(2p_H - p_{B_2})$. At $\bar{n}_d = 0.5$, the value of $[H^+]^2/B_2$ gives K'_f.

The instability or dissociation constant of the complex, $[MDiged]^{++}$, is given by

$$K=\frac{[M^{++}].[Diged]}{[M\ Diged^{++}]}$$

$$=\frac{[M^{++}].[Diged\ H_2^{++}]}{[MDiged^{++}].[H^+]^2}\times\frac{[Diged].[H^+]^2}{[Diged\ H_2^{++}]}$$

$$= k^*_1\,k^*_2/K'_f \quad .. \quad .. \quad (19)$$

Case II. When the acid disengaged by complex formation is more than $2C$ but less than $3C$, the pure metal ion and the complex $[(M\ Diged)(OH)_4]$ may be considered as almost absent. Therefore from (11), (12) and (14) assuming C_o and C_{h_2} equal to zero, we get

$$C_d=(3C-P-[H^+]+A-[OH^-]) + \frac{(X-C)\,(k^*_2[H^+]+2k^*_1k^*_2)}{k^*_1k^*_2+k^*_2[H^+]+2[H^+]^2} \quad (20)$$

$$C_{h_1}=(P-2C+[H^+]-A-[OH^-])-\frac{(X-C)\,(k^*_2[H^+]+2k^*_1k^*_2)}{k^*_1k^*_2+k^*_2[H^+]+2[H^+]^2} \qquad (21)$$

From this K_{h_1} can be obtained from

$$K_{h_1}=\frac{C_{h_1}\times[H^+]}{C_d} \qquad (22)$$

Case III. When the acid disengaged is greater than $3C$ but less than $4C$, the free metal ion, M^{++}, and the complex ion, $[MDiged]^{++}$, can be assumed to be almost absent and hence, $C_o=0$ and $C_d=0$, then the following relations may be obtained:

$$C_{h_1}=(4C-P+A-[H^+]+[OH^-])+\frac{(X-C)\,(k^*_2[H^+]+2k^*_1k^*_2)}{k^*_1k^*_2+k^*_2[H^+]+2[H^+]^2} \qquad (23)$$

$$\text{and } C_{h_2}=(P-3C+[H^+]-A-[OH^-])-\frac{(X-C)\,(k^*_2[H^+]+2k^*_1k^*_2)}{k^*_1k^*_2+k^*_2[H^+]+2[H^+]^2} \qquad (24)$$

and hence the second hydrolytic constant can be derived from

$$K_{h_2}=\frac{C_{h_2}\times[H^+]}{C_{h_1}} \qquad (25)$$

Plotting $\bar{n}_h$, the average hydroxyl group bound to the metal complex, which can be represented as $(C_{h_1}+2C_{h_2})/C$, against the corresponding p_H values, K_{h_1} and K_{h_2} can be evaluated when $\bar{n}_h=0.5$ and 1.5 respectively. From the values of K_{h_1} and K_{h_2}, the corresponding dissociation constants of the complex base, $k^*_{b_1}$ and $k^*_{b_2}$, can be deduced from the usual equation,

$$k^*_b=\frac{K_w}{K_h},\ K_w \text{ being the ionic product of water.}$$

In a similar manner the stepwise decomposition of the complex base [(M Diged) $(OH)_2$] in the presence of increasing amounts of acid may be represented as follows:

$$[(M\ Diged)\,(OH)_2]+H^+ \rightleftarrows [(M\ Diged)\,(OH)]^+ + H_2O \qquad (26)$$

$$[(M\ Diged)\,(OH)]^+ + H^+ \rightleftarrows [M\ Diged]^{++} + H_2O \qquad (27)$$

$$[M\ Diged]^{++} + 2H^+ \rightleftarrows M^{++} + [Diged\ H_2]^{++} \qquad (28)$$

and the respective equilibrium constants, K'_{h_2}, K'_{h_1} and K'_d are given by,

$$K'_{h_2}=\frac{[\{(M\ Diged)\,(OH)\}^+]}{[(M\ Diged)\,(OH)_2].[H^+]} \qquad (29)$$

$$K'_{h_1} = \frac{[\text{M Diged}^{++}]}{[\{(\text{M Diged})(\text{OH})\}^{+}].[\text{H}^{+}]} \quad .. \quad .. \quad (30)$$

$$K'_{d} = \frac{[\text{M}^{++}].[\text{Diged H}_2^{++}]}{[\text{M Diged}^{++}].[\text{H}^{+}]^2} \quad .. \quad .. \quad (31)$$

When a solution containing a known strength of the complex base $[(\text{M Diged})(\text{OH})_2]$ is titrated against a standard acid (HCl), the constants K'_{h_2}, K'_{h_1} and K'_{d} can be calculated from the measured p_H values of the mixture and the acid dissociation constants, k^*_1 and k^*_2, of the ligand in the following way.

Let C be the concentration of the complex base originally present and let C_{h_2}, C_{h_1}, C_d and C_o be the respective concentration of $[(\text{M Diged})(\text{OH})_2]$, $[(\text{M Diged})(\text{OH})]^{+}$, $[\text{M Diged}]^{++}$ and M^{++} present in the reacting mixture at any time, then,

$$C = C_{h_2} + C_{h_1} + C_d + C_o \quad .. \quad .. \quad (32)$$

The acid consumed by the reaction can be represented by $(A - [\text{H}^{+}])$, where A is the amount of the acid added;

$$A - [\text{H}^{+}] = C_{h_1} + 2C_d + 2B_o + 3B_1 + 4B_2 \quad .. \quad (33)$$

where B_o, B_1 and B_2 are the concentrations of Diged, $[\text{Diged H}]^{+}$ and $[\text{Diged H}_2]^{++}$ respectively.

$$\text{Again, } C_o = B_o + B_1 + B_2 \quad .. \quad .. \quad (34)$$

There may arise three cases under these circumstances :

Case I. When the acid used up is less than C, only the reaction (26) takes place and so the ions, $[\text{M Diged}]^{++}$ and M^{++}, and consequently Diged, $[\text{Diged H}]^{+}$ and $[\text{Diged H}_2]^{++}$ are absent. Assuming therefore C_d, C_o, B_o, B_1 and B_2 all to be negligibly small, we get from (32), (33) and (34)

$$C_{h_1} = A - [\text{H}^{+}] \quad .. \quad .. \quad (35)$$

$$C_{h_2} = C - A + [\text{H}^{+}] \quad .. \quad .. \quad (36)$$

Hence K'_{h_2} can be calculated from

$$K'_{h_2} = \frac{C_{h_1}}{C_{h_2} \times [\text{H}^{+}]} \quad .. \quad .. \quad (37)$$

Case II. When the acid consumed is more than C and less than $2C$, then the presence of $[(\text{M Diged})(\text{OH})_2]$, M^{++}, Diged, $[\text{Diged H}]^{+}$ and $[\text{Diged H}_2]^{++}$ may be assumed to be negligibly small. Then, from the set of equations (32—34), assuming C_{h_2}, C_o, B_o, B_1 and B_2 as zero, we get.

$$C_d = A - [\text{H}^{+}] - C \quad .. \quad (38)$$

$$C_{h_1} = 2C - A + [\text{H}^{+}] \quad .. \quad (39)$$

Hence, K'_{h_1} can be calculated from

$$K'_{h_1} = \frac{C_d}{C_{h_1} \times [H^+]} \qquad .. \qquad (40)$$

The above two constants can also be obtained graphically by plotting $\bar{n}_h$, the average number of hydroxyl groups bound to the complex molecule, which is given by $(C_{h_1}+2C_{h_2})/C$, against the p_H values and evaluating K'_{h_2} and K'_{h_1}, when $\bar{n}_h = 1.5$ and 0.5 respectively.

Case III. When the acid used up is more than $2C$ but less than $4C$, [(M Diged) $(OH)_2$] and [(M Diged) $(OH)]^+$ may be taken as practically absent; then from the equations 32, 33 and 34, we obtain

$$B_2 = \frac{[H^+]}{k^*_2 + 2[H^+]}(A - [H^+] - 2C) \qquad .. \qquad .. \qquad (41)$$

$$C_o = 1/2\ (A - [H^+] - 2C) + \frac{[H^+]\ k^*_2 + 2k^*_1 k^*_2}{2\ [H^+]\ k^*_2 + 4[H^+]^2}\ (A - [H^+] - 2C) \qquad (42)$$

$$C_d = 1/2\ (4C - A + [H^+]) - \frac{[H^+]\ k^*_2 + 2k^*_1 k^*_2}{2\ [H^+]\ k^*_2 + 4\ [H^+]^2}\ (A - [H^+] - 2C) \qquad .. \qquad (43)$$

Hence K'_d can be calculated from

$$K'_d = \frac{C_o \times B_2}{C_d \times [H^+]^2} \qquad .. \qquad .. \qquad (44)$$

The value of K'_d can also be obtained graphically by plotting $\bar{n}_d$, the average ligand bound to the metal atom, which is C_d/C, against $2p_H - pB_2$; K'_d being calculated from the value of the latter corresponding to $\bar{n}_d = 0.5$.

Incidentally, it may be stated that the constants K'_d, K'_{h_1} and K'_{h_2} are respectively the reciprocals of the previous constants K'_f, K_{h_1} and K_{h_2}.

EXPERIMENTAL

Diglycylethylenediamine dihydrochloride was prepared according to the method of Cottrell and Gill (*J.Chem. Soc.*, 1947, 129) and recrystallised from aqueous alcohol, m.p. 246° (decomp.). The free base was also prepared from the dihydrochloride as described by them and the product was recrystallised from hot butanol.

1. *Copper diglycylethylenediamine Chloride.*—An excess of freshly precipitated copper hydroxide, washed free from all impurities, was digested on the water-bath with diglycylethylenediamine dihydrochloride, when a deep blue solution was obtained. This was filtered from the excess of copper hydroxide and poured into an equal volume of dioxane. On keeping overnight, the substance separated out in beautiful blue flakes. These are very soluble in water, but insoluble in organic solvents. $\chi_g = 4.992 \times 10^{-6}$; $\chi_M = 1.541 \times 10^{-3}$; $\mu_B = 1.92$.

[Found : Cu, 20.51 ; Cl, 23.1 ; N, 18.21. $[(C_6H_{14}O_2N_4)Cu]Cl_2$ requires Cu, 20.59; Cl, 22.97 ; N, 18.15 per cent].

2. *Copper diglycylethylenediamine hydroxide* was obtained by treating the complex chloride solution with an excess of moist silver oxide. A trace of silver also went into solution by complex formation. This was removed by adding a little copper chloride solution drop by drop till the filtrate from the silver chloride precipitate was free from both Ag and Cl ions. The filtrate, which had a permanganate like colour, was then evaporated to dryness in vacuum over concentrated sulphuric acid. The complex base was then obtained in red-violet flakes.

It can also be obtained by digesting freshly precipitated copper hydroxide with a solution of the free reagent base.

The substance is soluble in water yielding a deep permanganate-red solution, which reacts alkaline (p_H 9.0). On heating with ammonium salts, it evolves ammonia and the solution assumes a deep blue colour. A similar blue colour is also obtained by passing CO_2 through the red solution. The solid red compound gradually turns blue in atmospheric air. $\chi_g = 3.881 \times 10^{-6}$; $\chi_M = 1.182 \times 10^{-3}$; $\mu_B = 1.72$. {Found : Cu, 19.97 ; N,17.56. $[(C_6H_{14}O_2N_4)Cu](OH)_2$, 2.5 H_2O requires Cu, 20.05 ; N, 17.6 per cent}. {Found (for the product dried at 110°) : Cu, 23.44 ; C, 26.8 ; H, 5.78. $[(C_6H_{14}O_2N_4)Cu](OH)_2$ requires Cu, 23.39 ; C, 26.5; H, 5.91 per cent}.

3. *Nickel diglycylethylenediamine chloride* was obtained like the corresponding copper salt by digesting an excess of nickel hydroxide with the hydrochloride of the reagent in aqueous solution. From the greenish blue filtrate, nickel diglycylethylenediamine chloride was precipitated as a sticky mass by the addition of alcohol. This was filtered and dried in vacuum. The substance forms a greenish blue hygroscopic powder, highly soluble in water. $\chi_g = 10.54 \times 10^{-6}$; $\chi_M = 3.202 \times 10^{-3}$; $\mu_B = 2.8$. {Found : Ni, 19.01 ; Cl, 23.1. $[(C_6H_{14}O_2N_4)Ni]Cl_2$ requires Ni, 19.31 ; Cl, 23.3 per cent}.

4. *Nickel diglycylethylenediamine hydroxide* was obtained by treating an aqueous solution of the complex chloride with an excess of moist silver oxide. From the yellow solution the last trace of silver was removed by careful addition of dilute nickel chloride solution till the filtrate became free from both Ag and Cl ions. This was then evaporated in vacuum and the residue was digested with absolute alcohol. The product was finally dried in vacuum over sulphuric acid.

The substance froms a very hygroscopic yellow powder, which turns greenish blue in atmospheric air. Its aqueous solution is strongly alkaline (p_H 9.3). $\chi_g = -0.6437 \times 10^{-6}$; $\chi_M = -0.1718 \times 10^{-3}$. {Found : Ni, 22.05 ; C, 26.5; H, 5.4 ; N, 21.11. $[(C_6H_{14}O_2N_4)Ni](OH)_2$ requires N, 21.9 ; C, 26.99 ; H, 5.28 ; N, 21.05 per cent}.

Magnetic susceptibilities of the substances were measured in a Gouy's balance.

Determination of the Instability Constants of the Metal Complexes

The following solutions were prepared :

(*i*) Copper chloride (0.05*M* in 0.01*M* free HCl), (*ii*) nickel chloride (0.05*M* in 0.01*M* free HCl), (*iii*) zinc chloride (0.05*M* in 0.0122*M* free HCl), (*iv*) cadmium chloride (0.05*M* in 0.044*M* free acid), (*v*) magnesium chloride (0.05*M* in 0.01*M* HCl). Merck's analytical reagents were used in all cases; (*vi*) ligand hydrochloride (0.05*M*) in molar KCl, (*vii*) caustic potash in *M*-KCl, freed from carbonate by treatment with baryta.

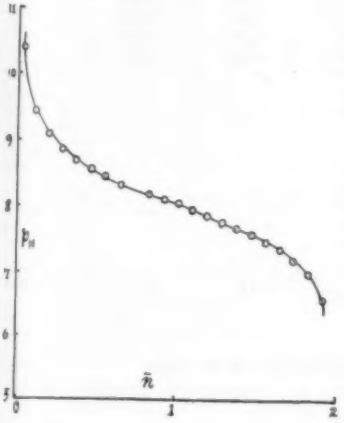
In all p_H measurements a Cambridge (bench type) p_H—potentiometer was used.

The method for the study of the formation constants of the metal complexes consisted in the addition of alkali to a solution of the metal chloride mixed with a little free hydrochloric acid and an excess of the reagent hydrochloride, and in measuring the p_H values of the solution after each addition.

In order to keep the ionic strength constant all the reactions were carried out in solutions containing KCl of 1 molar strength.

Fig. 1

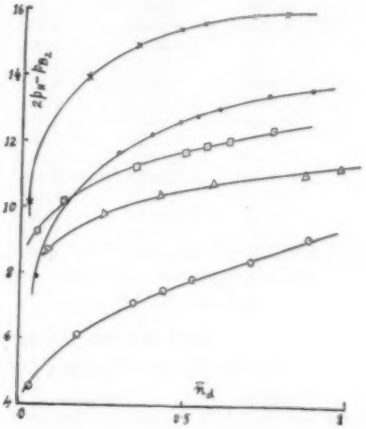
Titration curves of DigedH_2Cl_2 *with alkali.*



$\bar{n}$—av. no. of H^+ bound to the ligand base.

Fig. 2

Tirtration curves of DigedH_2Cl_2 *and* M^{++} *ions with alkali* (cf. Table II).



$\bar{n}_d$ = av. no. of the ligand (Diged) mols. bound to the metal ions.

[The curves from the top downwards represent respectively Mg, Cd, Zn, Ni and Cu ions.]

TABLE I

Acid dissociation constants of diglycylethylenediamine in salt solutions at 25°.

125 c.c. of 0.02M ligand dihydrochloride containing $BaCl_2$ (0.01M) and KCl (1M) titrated against 0.447M carbonate-free KOH solution (in M-KCl).

Alkali (moles/litre $\times 10^2$).	Strength of ligand (moles/litre $\times 10^2$).	p_H.	$\bar{n}$.	Alkali (moles/litre $\times 10^2$).	Strength of ligand (moles/litre $\times 10^2$).	p_H.	$\bar{n}$.
0.1781	1.992	6.520	1.91	2.0510	1.900	8.050	0.92
0.3555	1.976	6.950	1.82	2.2140	1.893	8.120	0.83
0.5312	1.968	7.150	1.73	2.3750	1.886	8.200	0.74
0.7053	1.960	7.310	1.64	2.5350	1.879	8.295	0.65
0.8781	1.953	7.410	1.55	2.6940	1.871	8.400	0.56
1.0480	1.945	7.525	1.46	2.8510	1.865	8.520	0.47
1.2180	1.937	7.620	1.37	3.0080	1.857	8.655	0.38
1.3900	1.929	7.710	1.28	3.1630	1.852	8.820	0.29
1.5560	1.923	7.800	1.19	3.3180	1.845	9.050	0.20
1.7230	1.915	7.890	1.10	3.4700	1.838	9.450	0.11
1.8890	1.907	7.970	1.01	3.6230	1.830	10.360	0.02
	$pk_2^*=7.63$			$pk_1^*=8.35$	$pk^*(av)=7.99$		

From the curve obtained by plotting $\bar{n}$ against p_H, the approximate values of k^*_1 and k^*_2 were obtained from the p_H values at $\bar{n}=0.5$ and $n=1.5$ respectively. By substituting these approximate values to the general equation, the more precise values for these were calculated (cf. Carlson, McReynolds and Verhoek, *loc. cit.*).

TABLE II

Formation and hydrolysis of copper diglycylethylenediamine complex.

25 c.c. of 0.05*M* of copper chloride in 0.01*M*-HCl and 50 c.c. of the reagent hydrochloride (0.05*M*) made up with KCl solution to 125 c.c. to make it 1 *M* in KCl.

Strength (in moles/litre×10²) of							
Alkali.	Metal.	Ligand.	Free acid.	p_H.	$2p_H - p_{B_2}$.	$\bar{n}_d$.	$\bar{n}$.
0.1781	0.9961	1.992	0.1992	3.130	4.55	0.027	..
0.5301	0.9881	1.976	0.1976	3.940	6.14	0.174	..
0.8764	0.9804	1.961	0.1961	4.470	7.15	0.348	..
1.0470	0.9766	1.953	0.1953	4.670	7.53	0.436	..
1.2170	0.9727	1.945	0.1945	4.850	7.86	0.525	..
1.5530	0.9651	1.930	0.1930	5.180	8.45	0.699	..
1.8850	0.9585	1.916	0.1916	5.565	9.10	0.879	..
2.2100	0.9506	1.901	0.1901	6.150	..	..	0.092
2.5300	0.9434	1.887	0.1887	6.500	..	..	0.399
2.6880	0.9397	1.879	0.1879	6.640	..	..	0.570
2.8450	0.9363	1.873	0.1873	6.780	..	..	0.708
3.1570	0.9294	1.859	0.1859	7.140	..	..	0.926
3.4630	0.9226	1.845	0.1845	7.510	..	..	1.030
3.7660	0.9158	1.832	0.1832	7.800	..	..	1.102
4.0630	0.9090	1.818	0.1818	8.040	..	..	1.216
4.3560	0.9024	1.805	0.1805	8.230	..	..	1.374
4.6460	0.8960	1.792	0.1792	8.450	..	..	1.526
4.9320	0.8898	1.779	0.1779	8.700	..	..	1.696
5.2130	0.8835	1.767	0.1767	9.140	..	..	1.914

TABLE III

Acid decomposition of copper diglycylethylenediamine hydroxide.

0.01162*M* complex base in 1*M*-KCl titrated against 0.1142 *M*-HCl (in *M*-KCl).

Acid (moles/litre×10²).	Complex (moles/litre×10²).	p_H.	$\bar{n}_h$.	$\bar{n}_d$.	$2p_H - p_{B_2}$.
0.0906	1.1510	8.85	1.922	..	..
0.2676	1.1320	8.65	1.762	..	..
0.4392	1.1150	8.50	1.605	..	..
0.5230	1.1070	8.47	1.528	..	..
0.6054	1.0980	8.44	1.448	..	..
1.0000	1.0590	7.77	1.055	..	..
1.1010	1.0510	7.56	0.953	..	..
1.2950	1.0280	7.02	0.740	..	..
1.5070	1.0070	6.60	0.503	..	..
1.7740	0.9797	6.29	0.189	..	..
2.1500	0.9417	6.00	..	0.857	9.12
2.3840	0.9177	5.66	..	0.699	8.76
2.5540	0.9007	5.37	..	0.581	8.31
2.6630	0.8896	5.12	..	0.502	7.88
2.8200	0.8736	4.90	..	0.385	7.53
3.0720	0.8480	3.87	..	0.181	5.58

TABLE IV

Initial concentrations before titration of the solutions employed.

(*a*) Formation experiments.

		Initial conc. (moles/litre×10²) of			
	Initial volume.	Metal.	Free acid.	Ligand.	Initial p_H.	KCl.
Copper	125 c.c.	1	0.1	2	2.77	1 *M*
Nickel	125	1	0.1	2	2.77	,,
Zinc	125	1	0.2440	2	2.7	,,
Cadmium	125	1	0.4444	2	2.43	,,
Magnesium	125	1	0.1	2	2.77	,,

(*b*) Decomposition experiments.

	Volume.	Complex base (moles/litre x 10^3)	p_H.	KCl.
Copper	125 c.c.	1.168	9.00	1 *M*
Nickel	125	1.104	9.30	1

TABLE V

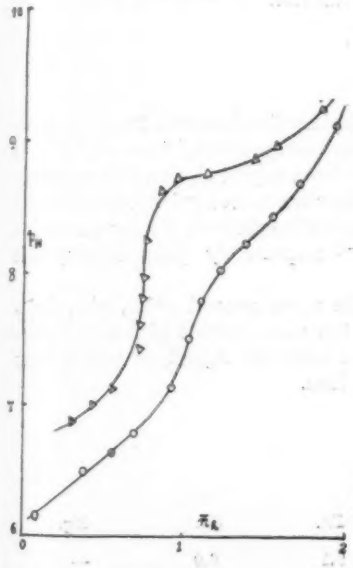
Values of the various constants.

	Copper.	Nickel.	Zinc.	Cadmium.	Magnesium.
pK'_1	7.85 (2)	10.56 (2)	11.67 (2)	12.65 (2)	15.44* (2)
log K'	7.87 (4)	10.56 (4)	..	..	..
pK	8.13	5.42	4.31	3.33	0.54*
pKh_2	8.43 (3)	8.94 (3)	..	..	..
pKh_1	6.58 (3)	7.04 (3)	..	..	..
$\log K'h_1$	6.59 (5)	7.03 (5)	..	..	..
$\log K\,h_2$	8.46 (5)	8.93 (5)	..	..	..
pk^*b_1	7.38	6.92	..	..	..
pk^*b_2	5.53	5.02	..	..	..

(2), (3) (4) and (5) indicate the Fig. No. of the curves from which the values were derived.

Fig. 3

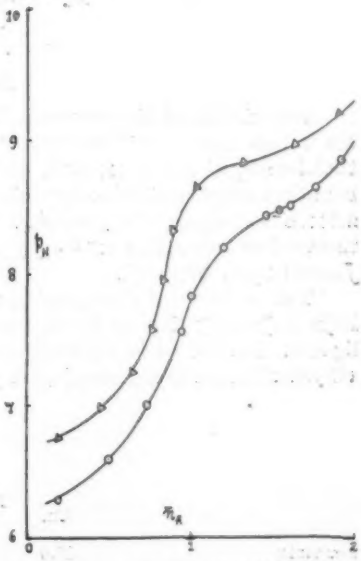
Titration curves showing hydrolysis of the complex (cf. Table II).



$\bar{n}_h$=av. no. of OH bound to the complex radical; upper—Ni, lower—Cu.

Fig. 4

Titration curves of the complex base with acid till neutralisation (cf. Table III).



$\bar{n}_h$=av. no. of OH bound to the complex radical; upper—Ni, lower—Cu.

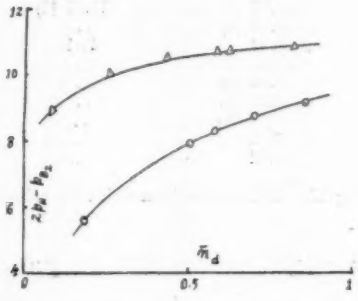
In the case of copper and nickel complexes determination of the instability constants was also made from a study of their decomposition by means of acids. For this purpose a solution of the copper or the nickel base in molar KCl was titrated against standard HCl (in *M*-KCl) and the p_H value of the solution after each addition was measured.

Acid dissociation constants of diglycylethylenediamine were determined by titrating with standard alkali a solution of the hydrochloride of the base in 1*M*-KCl containing 0.01*M*-$BaCl_2$ and measuring the p_H values after each addition.

The results of measurements are given in Tables I to V and represented graphically in Figs. 1-5.

Fig. 5

Tihation curves showing the decomposition of the complex
(cf. Table III).



$\bar{n}_d$ =av. no. of the ligand bound to the metal ion.
p_{B_2} = — log. of the ligand dihydrochloride conc.
[upper—Ni; lower—Cu]

DISCUSSION

The acid dissociation constants k^*_1 and k^*_2 of diglycylethylenediamine were found to have the values 4.467×10^{-9} and 2.344×10^{-8} respectively. The average value, $k^*_{av}=\sqrt{k^*_1 k^*_2}$, is therefore equal to 1.023×10^{-8}. This shows, as might have been expected, that it is a weaker base than ethylenediamine for which the corresponding values are 1.2×10^{-10}, 6.4×10^{-8} and 2.8×10^{-9} (Carlson, *et al., loc. cit.*). It is, however, somewhat stronger than glycine for which these values are 2.82×10^{-10}, 5.75×10^{-3} and 1.27×10^{-6} respectively (Das Sarma, this *Journal* 1952, **29**, 217).

The stability of the complexes determined follow the same general order, viz., Cu> Ni> Zn> Cd> Mg, as is the case with complexes of the above metals with many other ligands. The pK values for complexes of the above metals with this ligand, as well as with ethylenediamine and ammonia, are given below for comparison.

TABLE VI

	p_K values for complexes of				
	Cu.	Ni.	Zn.	Cd.	Mg.
Ammonia	12.6	7.8	9.1	6.9	—
Ethylenediamine	19.6	18.06	12.09	12.09	—
Diglycylethylenediamine	8.13	5.42	4.31	3.33	0.54

It shows that the ligand diglycylethylenediamine is a much weaker co-ordinating or complexing agent than even ammonia. This seems apparently to support Calvin and Wilson's suggestion (*J. Amer. Chem. Soc.*, 1945, **67**, 2003) about the relation between the basic character of the ligand and its complex forming capacity.

The character of the ligand as a weaker base and as a weaker co-ordinating agent is also evident from the fact that of the four co-ordinating or electron-donating nitrogen atoms, two are derived from the amido groups.

The hydrolytic constants K_{h_1} and K_{h_2} could be determined only for copper and nickel complexes. The cadmium and zinc compounds are more or less completely decomposed into the corresponding insoluble hydroxides above p_H 8. From these, the dissociation constants $k^*_{b_1}$ and $k^*_{b_2}$ of the complex bases were deduced.

The hydrolysis constants of the complex copper and nickel salts have been calculated on the assumption that the corresponding complex bases are very weak, and hence, occur almost in the undissociated state in aqueous solution. This may not be strictly correct. Nevertheless, that the ionic dissociation of the complex bases is strongly depressed in the presence of an excess of alkali is revealed by the colour change of the copper base with the increase of alkali added. The violet-red solution of the complex copper base assumes a deep pink tint like that of permanganate with an excess of alkali. The values of hydrolytic constants show that the copper complex ($K_{h_1}=2.63\times10^{-7}$ and $K_{h_2}=3.72\times10^{-9}$) is somewhat more hydrolysed than the corresponding nickel compound ($K_{h_1}=0.912=10^{-7}$ and $K_{h_2}=1.15\times10^{-9}$). The values of the corresponding dissociation constants $k^*_{b_1}$ and $k^*_{b_2}$ are 4.17×10^{-8} and 3.02×10^{-6} for Cu, and 12.02×10^{-8} and 9.55×10^{-6} for Ni. This shows that as a base the nickel complex is somewhat stronger than the corresponding copper base.

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STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER). PART VII. PROPERTIES OF JEOLIC ACID IN AQUEOUS SOLUTION

By S. N. Mukherjee and R. N. Rai Choudhury

Hydrogen-ion activity equivalent, conductance and cataphoretic velocity vary with the concentration of the jeolic acid solution in a manner similar to that of the arabic acid.

In previous communications of this series (Parts I-VI, this *Journal*, 1948, **25**) different behaviours and properties of the whole gum, purified by precipitation with alcohol, were studied with a view to determining primarily whether there was any aggregate formation in the aqueous solution of this gum, whether there was base-exchange and, if so, how far the latter could influence its viscous and electrochemical properties.

In the present paper the same study has been extended to the complex acid of gum jeol (previously referred to as the Jeolic acid in Part II) to ascertain how far the electrochemical properties of its aqueous solution are dependent on the concentration. Investigations have been carried out in the same line as indicated in the case of arabic acid (Mukherjee and Ghosh, this *Journal*, 1949, **26**, 81) with reference to the variations of hydrogen-ion activity, equivalent conductance and cataphoretic velocity with concentration.

Experimental

The jeolic acid solutions used in course of these investigations have been obtained by electrodialysis of the purified gum in absence of acids. It has been reported in Part IV of this series (this *Journal*, 1948, **25**, 333) that this jeolic acid can be obtained by mild hydrolysis of the gum by dilute H_2SO_4, or by electrodialysis of the gum in presence and also in absence of acids. The method of preparation based upon electrodialysis of the gum in absence of acids was preferred as in this process complications arising out of the introduction of an acid from outside were completely avoided. The acid was then precipitated by the addition of alcohol from a portion of the solution obtained by electrodialysis, washed with alcohol-ether mixture, dried and analysed by combustion yielding C, 39.1%, H, 7.6% and O,53.2%.

A stock solution of the acid of concentration 10 g. per litre was prepared from which other concentrations were obtained by dilution. Electrochemical properties studied here comprise the measurement of p_H, specific conductance and cataphoretic speeds (c.v.) at a temperature of $35° \pm 0.1$. Measurements of specific conductance were carried out at a frequency of 450 cycles approximately in a thermoionic valve oscillator. Cataphoretic measurements were carried out by the microscopic method in a flat glass cell of Freundlich and Abramson type. Ordinarily the particles could not be viewed quite clearly under the microscope (magnification about 600 times), but when the particles were in motion under an electric field, their motion could be followed. Potential gradient was measured by the help of Ohm's law from a knowledge of the specific conductance of the solution under examination.

H-ion activity or free acidity (a_H) was calculated from the p_H values in the usual manner with hydrogen electrode. Equivalent conductance cannot, however, be determined from specific conductance as the equivalent weight of the acid is not definitely known. Hence a quantity Λ has been calculated which refers to the conductance offered by that volume of the solution as contains 1 g. of the acid. This quantity will be strictly proportional to the equivalent conductance. Total titratable acidity (C_H) was determined by potentiometric titration of the acid with NaOH. Since C_H measures the concentration of the jeolic acid in equivalents (as obtained by titration with NaOH), the ratio a_H/C_H measures the hydrogen-ion activity per equivalent of the acid at any concentration and is a measure of the degree of dissociation or the activity coefficient (f) at that concentration.

DISCUSSION

Hydrogen-ion Activity.—Table I shows the variation of H-ion activity.

TABLE I

Jeolic acid solution.

Temp.=35°±0.1.

Conc. (g./litre)	p_H.	Free acidity or H-ion activity.	Total acidity ($C_H \times 10^4$ N)	a_H/C_H ratio ($=f$).	C.V. in cm./sec/volt/cm.$\times 10^4$.
0.7	3.93	1.17	6.31	0.185	1.79
1.0	3.66	3.21	9.01	0.245	2.34
3.0	3.28	5.31	27.10	0.197	2.07
4.0	3.20	6.38	35.85	0.171	1.74
5.0	3.17	6.81	45.16	0.157	1.50
7.0	3.07	8.57	64.0	0.134	1.24
10.0	2.88	15.32	89.6	0.174	1.26

The plot of a_H against concentration (c) shown in Fig.1 (curve 1) exhibits a small buffer region extending approximately from a concentration of 4 g. to 6 g. of the acid per litre. This presents a point of contrast of this acid with arabic acid where the a_H increases with concentration uneventfully along a smooth curve (Mukherjee and Ghosh, *loc. cit.*, p. 84, Fig. 2). Whether this peculiarity is in any way associated with the behaviour of the whole gum itself, which shows little variation of H-ion activity with concentration of its aqueous solution (Mukherjee and Rohatgi, this *Journal*, 1948, **25**, 342, Table III, columns 2 and 3), is difficult to ascertain, but they appear to be mutually suggestive.

FIG. 1

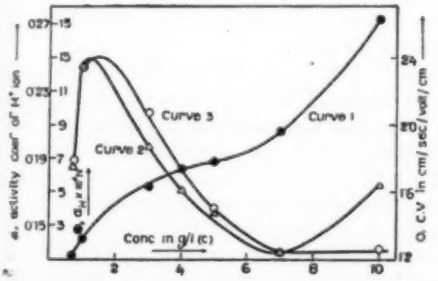
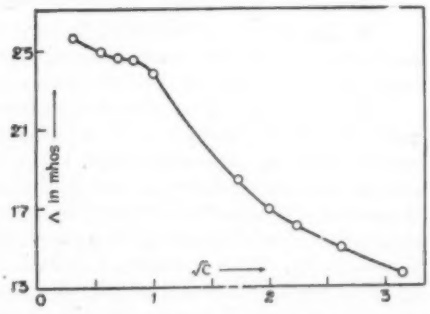


FIG. 2



The total acidity C_H, however, varies linearly with concentration but the ratio a_H/C_H shows a maximum and a minimum occurring at concentrations of 2.0 and 7 g. per litre of the acid respectively (vide Fig. 1, curve 2). In this respect the jeolic acid resembles the behaviour of the arabic acid which also shows a maximum and a minimum in the value of the ratio, at concentrations of about 1 g. and 24 g. respectively (Mukherjee and Ghosh, *loc. cit.*, Mukherjee and Bhowmik, this *Journal*, 1949, **26**, 152, Table I, column 5). Another interesting feature in this connection is that the value of this ratio, which serves as an approximate measure of the degree of dissociation of the acid, is quite small, the maximum value observed being near about 25% at 1% concentration of the acid. This apparently signifies that the acid is a weak one having quite a low degree of dissociation, although the potentiometric titration curve reveals the character of a strong acid which will be discussed in the next communication.

Equivalent Conductance.—In the following table the data for specific conductance and equivalent conductance (Λ) have been shown (Table II).

TABLE II

Jeolic acid solution.

Temp.=35°±0.1. Sp. cond. of water used=1.2×10^{-6} mho at 35°.

Conc. (g./litre)	C.	Specific conductance×10^3. (obs.).	*(calc. from a_H).	Equiv. cond. in g./litre.
0.1	0.32	0.26 mho	—	2.56 mho
0.3	0.56	0.75	—	2.49
0.5	0.70	1.23	—	2.46
0.7	0.83	1.71	2.62 mho	2.45
1.0	1.00	2.38	3.60	2.38
3.0	1.73	5.53	10.80	1.34
4.0	2.00	6.74	14.34	1.69
5.0	2.24	8.00	18.06	1.60
7.0	2.65	10.44	25.60	1.49
10.0	3.16	13.57	35.84	1.36

* a_H values have been taken from Table I.

Plotting Λ against $\sqrt{C}$ a straight line graph is expected from Onsager's equation which connects Λ with $\sqrt{C}$ by the equation, $\Lambda_c = \Lambda_o - k\sqrt{C}$, where Λ_o is the value of Λ at infinite dilution and k, a constant giving the slope of the line. The actual graph is shown in Fig. 2. from which the following interesting observations are noted.

(*a*) Λ decreases almost linearly with $\sqrt{C}$ up to a concentration of 1 g./litre (approx.). Beyond this point the diminution is more rapid. There is thus a kink in the curve which has been regarded by Hartley as a feature characterising the starting point of aggregates formation in solutions of colloidal electrolytes. If the kink be regarded as indicative of the starting point of aggregate formation, the concentration corresponding to the kink does not tally with the maximum of the $(a_H/C_H{}^- C)$ curve.

(*b*) Λ does not appear to pass through a minimum.

(*c*) The curve extrapolated to zero concentration gives low values for the equivalent conductance calculated on the basis of the equivalent weight obtained by titration with NaOH, even lower than that of hydrogen ions alone at infinite dilution.

Moreover, as will be evident from columns 3 and 4 of Table II, the specific conductances calculated from the hydrogen-ion activity at the corresponding concentrations are always greater than the observed values. Of course, in these cases calculations have been carried out on the assumption that the equivalent conductance of H-ions at 35° is 400 mho (cf. Glasstone, "Electrochemistry of Solutions", 1937, p.72 ; Int. Crit. Tables, 1929, VI, 259), and that it is not influenced by presence of other ions in the solution (cf. independent migration of ions). How far such calculations are justified in these cases awaits clarification. This discrepancy between calculated and observed values of specific conductance at different concentrations are in agreement with those observed in the case of arabic acid (cf. Mukherjee and Ghosh, this *Journal*, 1949, **26**, 84, Table II, columns 3 and 5) but is just the reverse of what has been noted in the case of yeast nucleic acid (cf. Mukherjee and Sarkar, this *Journal*, 1947, **24**, 72, Table V, columns 3 and 4).

Cataphoretic Mobility.—Variations of cataphoretic speeds with concentration have been shown in the last column of Table I and graphically represented in Fig. 1 (curve 3).

The graph passes through a maximum at a concentration of 1.6 g./litre and reaches a constant value at higher concentrations. Thus, the concentration, where the maximum occurs in this case, is close to that where the kink is observed to appear in Λ—$\sqrt{C}$ curve viz., at 1 g./litre. The curve appears to be similar in nature to that of arabic acid (cf. Mukherjee and Ghosh, *loc. cit.*).

The authors' thanks are due to Dr. H. L. Roy for his keen interest.

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STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER), PART VIII. INTERACTION OF JEOLIC ACID WITH ACIDS AND BASES

By S. N. Mukherjee

The jeolic acid behaves like arabic acid (already reported) in its interaction with bases, acids and neutral salts, the difference being essentially in the degree in which the effects appear. It is a monobasic acid, having an equivalent weight of 1200, and dissociation constant of the order of 10^{-4} i.e., of weak character, although its potentiometric titration curve is like that of HCl. Total acidity varies with the nature of the cation used for titration. It shows reserve acidity in its interaction with acids and the existence of base-exchange when treated with neutral salts.

As pointed out towards the end of Part VII of this series (this *Journal*, 1953, **30**, 201), interaction of jeolic acid with acids, bases and neutral salts is worth investigation to clarify the behaviour of this acid, forming a colloidal solution in water. The present study comprises the determination of total acidity, basicity, the dissociation constant and the equivalent weight of the jeolic acid both by potentiometric and conductometric titrations with bases and also the estimation of the changes in the hydrogen-ion activity of the solution by the addition of acids and neutral salts.

The object of this investigation is to examine how the nature of the cation influences such properties and also to detect the existence and magnitude of the base-exchange occurring in this system.

Experimental

Two different specimens of jeolic acid were selected for this investigation : (1) A solution of jeolic acid obtained by electrodialysis in absence of acids and (2) a solution obtained by electrodialysis in presence of acids (for procedure of electrodialysis vide this series, Part IV, this *Journal*, 1948, **25**, 333). The concentration of these acids was always 1% (10 g./litre of solution).

All measurements were carried out at a temperature of 35° ± 0.1. Equilibrium water having specific conductance of 1.3×10^{-6} mhos was used throughout.

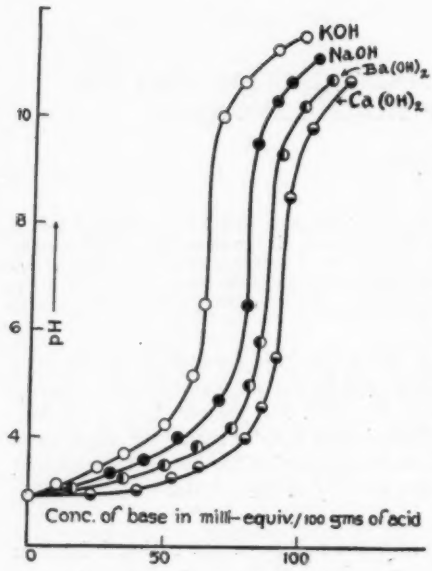
Potentiometric measurements were carried out with the help of hydrogen electrodes with necessary precautions mentioned by Mukherjee and Sarkar (this *Journal*, 1947, **24**, 65). Conductometric measurements were carried out as usual at a frequency of 440 cycles.

Four different bases viz., KOH, NaOH, $Ca(OH)_2$ and $Ba(OH)_2$ were studied and solutions of these bases were always prepared in carbon dioxide-free water.

Potentiometric Study with Bases

Titration curves with the different bases mentioned above for specimen (1) have been given in Fig. 1. These curves are very much similar to those of the arabic acid (cf. Mukherjee and Ghosh, this *Journal*, 1949, **26**, 277). They present the nature and shape of a strong monobasic acid with only one inflexion and the p_H of neutralisation is about 7.2. The acid of specimen (2) behaved exactly similarly, and the titration curves have not therefore been shown.

FIG. 1



The total acidity expressed in terms of milliequivalents of the base per 100 g. of the acid was not a constant quantity but varied with the nature of the base used for titration in the same manner as in arabic acid solutions, the only difference being in the relative cationic order : $Ca(OH)_2 > Ba(OH)_2 > NaOH > KOH$, the last one giving an abnormally low total acidity (vide Mukherjee and Ghosh, *loc. cit.*). The actual figures are shown in Table I. The cationic order in arabic acid was $Ca(OH)_2 > Ba(OH)_2 > KOH > NaOH$.

TABLE I

Sols.	Total acidity in m.e. of base/100 g. of acid. KOH.	NaOH.	$Ba(OH)_2$.	$Ca(OH)_2$.
Specimen 1 ..	59	79	88.5	96
Specimen 2 ..	62	81	90.0	95.0

It may be mentioned here that although the total acidity changes with the nature of the cation of the base used for titration, the differences are moderate and that it is independent of concentration of the acid as observed by titration with the above bases at different concentrations of the jeolic acid*.

Conductometric Study with Bases

Conductometric titration curves of specimen (1) have been shown in Fig. 2. These curves show two inflexion points, the first inflexion occurs at almost the same amount of base in all the cases and corresponds approximately to the neutralisation of the free acidity (for arabic acid vide Mukherjee and Ghosh, *loc. cit.*). A summary of the observations has been presented in Table II of jeolic acid solution, specimen (1).

TABLE II

Bases.	a_H from p_H $\times 10^4$ N.	m. equiv. of base corresponding to 1st inflexion.	Total acidity in m. equiv. base per 100 g. of acid from 2nd inflexion.
KOH	10.72	11.51	80
NaOH	,,	11.72	80
$Ba(OH)_2$	,,	15.05	89
$Ca(OH)_2$	,,	15.71	96

* These data have not been presented here as they are exactly of the type shown in the case of arabic acid by Mukherjee and Ghosh (this *Journal*, 1949, **26**, 81).

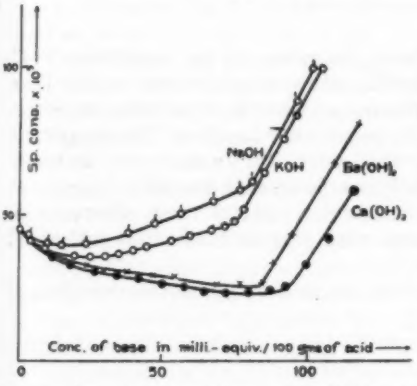
The second inflexion obviously yields the total acidity. Evidently, total acidities obtained from potentiometric and conductometric titrations agree with each other. The base corresponding to the first inflexion point tallies fairly well with the hydrogen-ion activity of the solution at least in the case of KOH. With $Ba(OH)_2$ and $Ca(OH)_2$ there has been a slight increase which will be understood in the light of the discussions brought forth in connection with the effect of neutral salts.

The nature of the titration curves simulates that of a weak acid, specially beyond the first inflexion point. The dissociation constant of the acid, as calculated in 1% solution by the formula

$$K = \frac{(a_H)^2}{C_H - a_H}$$

comes up to 3.4×10^{-4} where a_H corresponds to the hydrogen-ion activity and C_H to the total acidity. These are obtained from the first and second inflexion points of the conductometric titration curves. The equivalent weight of the acid calculated from titration with NaOH is about 1200 which is practically equal to that of arabic acid calculated on the same basis. The order of the dissociation constant reveals the acid to be of weak nature although the potentiometric titration curve is like that of a strong acid.

FIG. 2

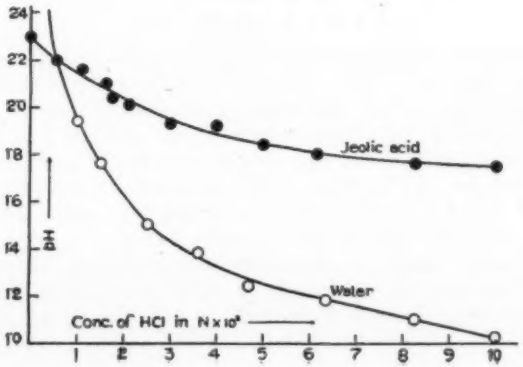


Interaction with Acids

The next point investigated was to examine how these systems interact with acids. For this reason the jeolic acid was titrated with a standard HCl solution and the variation of p_H with increasing concentration of HCl was carefully noted by the potentiometric method and compared with such variation in the case of water.

The result of this has been graphically shown in Fig. 3. The behaviour of the jeolic acid is very much like that of arabic acid (cf. Mukherjee and Ghosh, *loc. cit.*). The difference lies only in the degree of buffering in the two cases. The jeolic acid appears to have greater buffering properties, p_H remaining very little altered even with the addition of a considerable quantity of the acid. This in a way supports the view that the acid probably remains in part in the non-dissociated state which by suitable adjustment serves as a reserve.

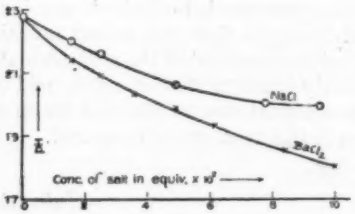
FIG. 3



Interaction with Neutral Salts

The total acidity of the jeolic acid, as observed by titration with bases having different cations, have been found to be different as already stated (vide Table I). These observations first indicated that most probably there might be some base-exchange phenomenon connected with these systems and different cations possessed different base-exchange capacities. This point has been directly put to test by examining the interaction of this jeolic acid with different salts having cations of different valencies. The scope of the investigation comprises, in this case, the variation of hydrogen-ion activity with the addition of increasing amounts of the salts : NaCl and $BaCl_2$.

FIG. 4



Results represented in Fig. 4 indicate that $BaCl_2$ depresses the p_H more than NaCl which perfectly fits in with our observation that $Ba(OH)_2$ shows a higher total acidity than NaOH in both potentiometric and conductometric titrations. $Ba(OH)_2$ thus liberates greater amount of hydrogen ions and thus exhibits a higher base-exchange capacity. The magnitude of this base-exchange capacity is, however, of a very small order. The anomaly viz., a slightly higher amount of the base is necessary at the first inflexion point with $Ba(OH)_2$ than what corresponds to the free acidity (a_H) is also understood in the light of these observations, because it appears that there is a slight base-exchange with this acid which is influenced differently by the different cations.

The author's best thanks are due to Dr. H. L. Roy for his keen interest in this piece of work.

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COPE-KNOEVENAGEL REACTION DYNAMICS. PART I. NATURE OF THE SECOND SOLVENT AND ITS ROLE

By Chittaranjan Raha

The yield of condensation products in a Cope-Knoevenagel reaction is correlated with the boiling point, the miscibility with water and the electron-releasing capacity of the second solvent used in such reactions. A low boiling, immiscible and low electron-releasing solvent ensures a higher yield. A synthesis of a thioether is described.

Knoevenagel showed that the condensation of reactive methylene compounds with carbonyl compounds could be effected in the presence of weak bases or their salts (*Chem. Zentrl.*, 1905, **76,** II, 179, 726, 1071). This was not of general applicability until Cope *et al.* (*J. Amer. Chem. Soc.*, 1937, **59,** 2327) found that the maximum yield was obtained only when the reaction was carried out in presence of acetic acid and the water formed was continuously removed by slow distillation. The acetic acid is supposed to act as the ionising solvent and to catalyse enolisation. Alexander ('Principles of Ionic Organic Reactions", John Wiley & Sons, Inc., N.Y., 1950, p. 183) mentions acetamide in acetic acid as the best catalyst. However, Cope (*J. Amer. Chem. Soc.*, 1941, **63,** 3452) later introduced a second inert and immiscible solvent for the removal of water formed *in situ* and found ammonium acetate as the best agent (cf. Cragoe *et al.*, *J. Org. Chem.*, 1950, **15,** 381). This modification by Cope of the main Knoevenagel procedure has been named the Cope-Knoevenagel reaction.

As the second solvent Cope *et al.* (*loc. cit.*) have recommended benzene. Since then several other solvents have been employed for the same purpose. These include toluene (Birch and Robinson, *J. Chem. Soc.*, 1942, 488) and chloroform (Wideqvist, *Acta Chem. Scand.*, 1949, **3,** 303). Cragoe *et al.* (*loc. cit.*) used *cyclo*hexane, benzene, toluene and xylene in a condensation reaction between benzophenone and ethyl cyanoacetate. They observed that the reaction rate, as indicated by the formation of water, increased and the yield of alkylidene ester decreased with an increase in the boiling point of the solvent. The low yield was attributed by these workers to the dehydration of the ammonium acetate to acetamide, which was not a catalyst for the condensation reaction in question. The high boiling point of the solvent is obviously responsible for rapid dehydration of ammonium acetate, and hence, it partially explains the low yield obtained with high boiling liquids.

However, the function of the second solvent in these types of reaction does not seem to have been fully realised. It is the purpose of this paper to obtain quantitative data on the condensation reaction between ethyl cyanoacetate and ethyl levulinate according to Cope-Knoevenagel using a number of solvents and under more or less identical experimental conditions.

Experimental

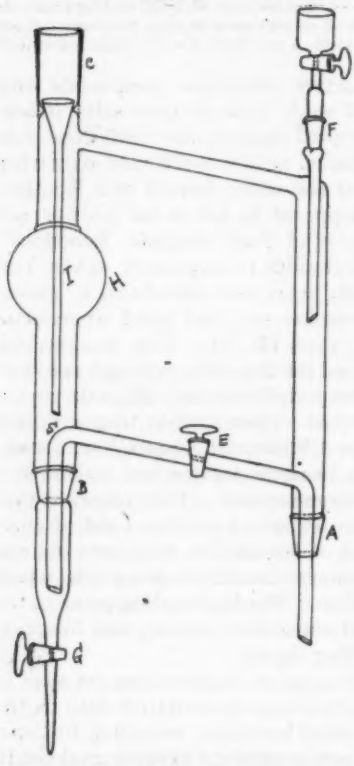
The solvents used were purified according to the directions prescribed by Fieser ("Experiments in Organic Chemistry", D. C. Heath and Co., New York, 1941, p. 357). The levulinic ester was prepared by esterifying crude levulinic acid with double distilled alcohol and concentrated sulphuric acid (*d* 1.84), the ester was worked up in the usual manner, re-esterified and distilled. The fraction of the ester of b.p. 206° was used in the investigation. The other reagents used were ethyl cyanoacetate (B.D.H.) fraction of b.p. 206-208°, ammonium acetate (E. Merck, Darmstadt, Germany) and glacial acetic acid (B.C.P.W.), b.p. 118°.

The thioether used as a second solvent in one investigation was prepared by a modification of the procedure described by McAllan *et al.* (*J. Amer. Chem. Soc.*, 1931, **73,** 3627); when the solvent was changed from water to alcohol the yield was noticed to drop from the almost theoretical value (as obtained by McAllan *et al.*) to 65% of theory. But the yield

again reached a theoretical value if some powdered potassium iodide was added. Most probably the potassium iodide acts by an ionic antagonism principle. The thioether prepared by this method had b.p. 92-93° and $n^{28.5}_{D}$ 1.4345.

A special apparatus (Fig. 1) had to be devised for studying reactions with solvents, both lighter and heavier than water. This apparatus is a modification of the one described earlier by the author (this *Journal*, 1953, **30**,129). The present apparatus acts by a siphon principle.

FIG. 1



In carrying out a reaction in presence of a solvent lighter than water, e.g., benzene, the flask is attached to A. The azeotropic mixture passes up, condenses in the condenser attached to C, falls along I, a thin funnel supported on a number of teeth in C and separates into two layers. The lower aqueous layer is frequently taken out by the stop-cock G and the upper layer of the immiscible solvent returns in the reaction flask along the siphon S.

For a solvent heavier than water, e.g., chloroform, mixed vapours from the reaction flask at A pass up into the condenser at C. The condensates fall along I and separate into an upper layer of water which is kept confined in the flask H and the lower layer of the heavier solvent returns along S into the reaction vessel. The water is taken out after the reaction is complete.

This apparatus may be used for the extraction of liquids with lighter or by heavier solvents. The case of the lighter solvents has been previously described (*loc. cit.*). With heavier solvents, however, an aqueous solution, the volume not exceeding that of H, can be extracted. At the outset of any operation, the flask with the solvent is attached to A. Another flask with the same solvent is placed at B. The stop-cock E remains closed and the aqueous solution is now poured in the bulb H. A certain amount of the solvent is also poured into it such that the zone of separation is above the siphon height S. The reflux of the solvent in the flask at A begins and after a few minutes the stop-cock E is regulated in such a manner that the solvent level is always above S. After the necessary period of extraction the solvent is allowed to flow into the flasks.

Procedure.—Ethyl levulinate (14.4 g., 0.1*M*), ethyl cyanoacetate (11.2 g., 0.1*M*), ammonium acetate (1.9 g., 0.025 *M*) and glacial acetic acid (6 ml., 0.1*M*) together with the second solvent (75 ml.) were refluxed for 3 hours at temperatures suitable for a constant reflux. In each case the cold reaction mixture was washed with three successive 25 ml. portions of water. The residual oil after the removal of the solvent was fractionated under vacuum. The fraction of b.p. 153-54°/5 mm. was collected (cf. Banerjee, this *Journal*, 1940, **17**, 423 gives b.p. 154-160°/5.5 mm.). The yields of the product obtained under more or less identical experimental conditions are presented in Table I (A).

Cragoe's technique (*loc. cit.*) of adding the catalyst in instalments was employed in some of the experiments; Table I (B) records the yields of the product obtained in the reactions in which the total amount (1.9 g.) of the catalyst was added in three instalments, each at an

TABLE I

	Solvents	Yield. A	Yield B
1.	Ether	6.7 g	..
2.	Thioether	7.6	..
3.	*n*-Hexane	14.8	13.3 g.
4.	Petrol ether (60°-80°)	14.8	13.7
5.	Chloroform	15.3	13.6
6.	Carbon tetrachloride ..	11.4	13.0
7.	*cyclo*Hexane	12.1	15.4
8.	Dioxane (75 ml.) + benzene (75 ml.) ..	0	..
9.	Acetic anhydride	0.8	..
10.	Benzene	17.8;17.5;17.9	14.5
11.	Toluene	16.1;15.5;15.8	13.5
12.	Xylene	11.5;11.9,11.3	10.5
13.	Benzene (37 ml.) + toluene (37 ml.) ..	11.3	10.9
14.	Benzene (60 ml.) + toluene (15 ml.) ..	12.6	..
15.	Benzene (60 ml.) + xylene (15 ml.) ..	12.0	..
16.	Benzene (50 ml.) + *tert.*-BuOH (25 ml.) ..	12.2	..
17.	Benzene (50 ml.) + *tert.*-BuOH (75 ml.) ..	2.3	..
18.	Toluene (37 ml.) + xylene (37 ml.) ..	11.4	10.8
19.	Xylene (50 ml.) + benzene (25 ml.) ..	12.1	12.6
20.	Xylene (50 ml.) + toluene (25 ml.) ..	12.3	11.4
21.	Benzene (75 ml.) + anisole (10 ml.) ..	15.4	..
22.	Benzene (75 ml.) + anisole (46 ml.) ..	11.6	..
23.	Without any solvent	3.8	..

interval of 45 minutes. The total time of reflux was the same as in the other cases viz., 3 hours. The yields in most cases are lower than that obtained with the catalyst added in one lot. The formation of high boiling by-products was encouraged by Cragoe's technique. In the case of camphor, however, yield of the condensation product always exceeded that obtained by Cragoe *et al.* themselves of larger amounts of the catalyst were used. Experimental data regarding this and a plausible explanation thereto will form a part of a future communication.

DISCUSSION

The essential prerequisite for ionic organic reactions is that the components must be soluble in the solvent used. It has been found that the yields obtained in *n*-hexane, petroleum ether (6.p. 60°-80°), carbon tetrachloride and *cyclo*hexane, used as the second solvent, were much below those obtained in the aromatic hydrocarbon solvents. In the former, the whole system remains inhomogeneous which is not the case with chloroform in which the yield is more or less higher. Similar poor yields or none at all are obtained with ether or dioxane-benzene mixture as the second solvent. Without a second solvent whatsoever the yield is low (3.8 g.). The removal of the water formed therefore seems essential. The more efficient the second solvent is in this respect, the better the yield. The failure of the oxo-ethers to remove water may be responsible for the poor yield obtained with them. However, a poor yield obtained in thioether in which water is insoluble makes the problem of removal of water a doubtful one. A glaring case which makes it still more doubtful is the negligible yield obtained with acetic anhydride as the second solvent. In fact, almost no reaction takes place, not even acetylation of the carbonyl compound used.

According to Cragoe *et al.* (*loc. cit.*) the boiling point of the second solvent is one of the factors determining the yield of the product. This is not borne out by the above experiments in which the boiling points of the solvents, viz., *n*-hexane, petroleum ether (60°-80°), carbon tetrachloride and *cyclo*hexane, are close to that of benzene ; but it is benzene which gives the highest yield.

The boiling point therefore appears not to be the sole deciding factor. The above solvents are not inert but, in fact, differ considerably as regards their electron-releasing capacity. On this basis it is found that the yield is lower, the greater the electron-releasing capacity of the second solvent, whether it is immiscible with or reactive towards water. Whenever the yield is low, either the unreacted components are left behind or high boiling reaction products are formed. The high boiling point of the second solvent probably lowers the yield indirectly through the formation of high boiling by-products, the amount of which increases with the boiling point of the second solvent. The yield data obtained with benzene, toluene and xylene confirm this (Table I). It should be mentioned that the electron-releasing capacity of these solvents are also in the order : xylene>toluene>benzene (Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, 1943, p. 91), the same order in which the yields increase. This point is further corroborated by the experiments with mixed solvents (Table I). They are composed of varying proportions of benzene, toluene and xylene and such electron-releasing liquids like *tert.*-BuOH or anisole. For instance, 1 : 1-benzene-toluene mixture gave a lower yield than the 4 : 1-benzene-toluene mixture. In the latter, if toluene was replaced by xylene, the yield dropped but slightly. An 1 : 1 xylene-toluene mixture gave almost the same yield (11.4 g.) as the 1 : 1 mixture of benzene and toluene (11.3 g.), 2 : 1-xylene-benzene and 2 : 1-xylene-toluene also gave almost the same yield although it should have been less in the latter.

The yield of product dropped with increasing proportions of *tert.*-BuOH added to benzene. The greater solubility of water, however, in *tert.*-BuOH should not be overlooked; but the yield is low even if water-immiscible anisole is added to benzene in place of *tert.*-BuOH.

The nature of the second solvent is concluded to greatly influence the formation of the product in the Knoevenagel-Cope reaction. Of all other properties of the second solvent, its boiling point, miscibility with water, and the electron-releasing capacity have been found to be correlated with the yield of the condensation product. For instance, a low boiling solvent ensures a higher yield by suppression of by-products. The immiscibility of the solvent with water and a low electron-releasing capacity are also favourable for higher yields.

Thanks are due to Dr. D. M. Bose, Director of the Institute and to Dr. J. K. Chowdhury, Head of the Department, for their interest and encouragement in this work.

Thanks are also due to Dr. D. K. Banerjee, Professor of Organic Chemistry, College of Engineering & Technology, Jadavpur, and to Dr. S. K. Mukherjee, Department of Applied Chemistry, Calcutta University, for their valuable suggestions and enlightening criticisms.

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Messrs. G. D. A. Chemicals Ltd., Calcutta maintained a constant supply of levulinic acid used in this work.

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INTERFACIAL TENSION OF ALIPHATIC ALCOHOLS AND AROMATIC LIQUIDS WITH SURFACE ACTIVE AGENTS. PART I

By Miss Hemlata J. Kazi and C. M. Desai

Measurements of the interfacial tension of some alcohols and aromatic liquids have been carried out against soap solutions. The tension at the oil droplet interface with increasing soap concentration is initially found to fall rapidly for dilute solutions, and thereafter reach a limiting value, when further increase in soap concentration has practically no effect, except in cases of *n*-hexyl and *sec.*-octyl alcohols which show a maximum in dilute soap solutions, followed by a rapid lowering.

Lowering of interfacial tension of organic liquids brought about by soaps and such substances is generally necessary for their emulsification. Soap solution has a low surface tension which together with the adsorbed interfacial film, contributes to its emulsifying property (Donnan, *Kolloid Z.*, 1910, 208; Bancroft, *J. Phys. Chem.*, 1915, **19**, 275 ; Harkins, *J. Amer. Chem. Soc.*, 1917, **39**, 541 ; Wilson, *J. Chem. Soc.*, 1934, 1360 ; McBain, "Colloid Science", 1950)

The effect of hydrolysis of soaps has been investigated by various workers (Harkins and Clark, *J. Amer. Chem. Soc.*, 1925, **47**, 1854 ; Powney, *Trans. Faraday Soc.*, 1935, **31**, 1510). Traces of free alkali first raise the surface tension to a maximum and then with further increase in alkali concentration, it decreases slowly and almost linearly. Addition of alkali suppresses hydrolysis, and the adsorbed layer consists of neutral soap which gives the maximum tension, while acid soap lowers the tension, as it is more strongly adsorbed than a neutral soap.

Surface tension curves have been classified according to three types (McBain *et al.*, *Kolloid Z*, 1937, **78**, 1). In type I, surface tension of the solvent is increasingly lowered with increasing concentration of the solute. This is the commonest case. In type II, surface tension is increased, though not to a great extent, with increasing concentration of the solute. In type III, there is a very great lowering of surface tension in a very dilute solution, the surface tension thereafter remaining approximately constant, or even, passing through a minimum, followed by a shallow maximum, but still at a value far below that of the solvent. In contrast to surface tension, the interfacial tension between two liquids is often reduced to nearly zero by the addition of a surface active agent. Sometimes, however, the behaviour may be similar to that of the three types mentioned.

Experimental

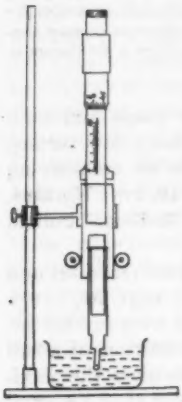
The liquids selected were as follows : *n*-butyl, *iso*butyl, *iso*amyl, *n*-hexyl and *sec.*-octyl alcohols and benzyl alcohol, methyl and ethyl benzoates, benzyl benzoate and hexane. Many of the liquids were from reliable manufacturers, such as Schering-Kahlbaum and E. Merck. They were, however, treated with sodium carbonate, washed with distilled water, dried and distilled under reduced pressure and the middle fractions were used for the purpose. The specific gravities of the liquids were determined using a calibrated 25 c.c. bottle and values obtained at 30° were used in the calculation of their interfacial tension. The substances used to lower the surface tension were sodium oleate, potassium oleate, with excess of acid and alkali, and saponin. They were prepared and purified by the usual methods.

The drop volume method using a microsyringe (Burroughs and Wellcome) was adopted throughout to determine the interfacial tension of liquids against water and soap solutions. The syringe was scrupulously cleaned by means of alcohol, soap and distilled water and then dried before each measurement. It was then filled with the liquids and kept vertically with the tip at the definite depth in the aqueous medium in the container. By the careful working

of the screw cap, the drops with maximum possible size were slowly allowed to be formed covering the entire tip. All measurements were taken under identical conditions at a temperature 30° (±1.0). The measurements were thrice repeated and the mean value was corrected by Harkin's factor (*J. Amer. Chem. Soc.* 1919, **41,** 499).

The arrangements of the apparatus is shown in Fig 1.

FIG. 1



The motion of the piston in the barrel (capacity, 1 c.c.) of the syringe is governed by the micrometer screw head. Each division on the barrel corresponds to a volume of 0.04 c.c. and each sub-divison on it is further calibrated by means of the micrometer screw to read 0.0004 c.c. The syringe with the liquids was clamped vertically with its tip pointing downwards for liquids heavier than water (Fig. 1), and the tip pointing upwards for those lighter than water. In the latter case, the barrel was fitted in the container holding aqueous medium by means of a tightly fitting rubber bung. In the case of liquids partly miscible with water, if the syringe be filled with such a liquid, the liquid often forms a continuous stream, instead of drops. If, however, the solubility of water in liquid is considerably less than that of liquid in water and water is filled in the syringe, water may give drops, and thus the tension of water against the liquid can be measured.

The variation in the interfacial tension of liquids with change in the soap concentrations ranging from $0.234\times10^{-3}M$ to $14.79\times10^{-3}M$ has been studied and the results are shown in Table I and Figs. 2 and 3.

TABLE I

Sodium oleate.	Interfacial tension depression (dynes/cm.) *n*-BuOH.	*iso*BuOH.	*iso*Amyl alcohol.	*n*-Hexyl alcohol.	*sec.*-Octyl alcohol.
0.000 $M\times10^3$	3.021	2.406	5.231	8.239	10.60
0.246	—	—	4.998	8.851	11.50
0.493	2.767	2.338	4.863	9.105	13.77
0.738	—	—	—	8.614	—
0.986	2.537	2.103	4.634	8.239	14.99
1.479	2.410	2.098	4.413	7.769	17.73
1.968	2.354	1.832	4.195	7.278	16.21
2.460	2.105	1.766	3.788	—	15.26
2.950	—	—	3.659	—	13.91
3.940	—	—	—	5.658	—
4.930	1.935	1.646	3.348	—	11.76
9.860	—	—	3.073	—	10.60
14.790	—	—	2.877	4.461	6.76

The interfacial tension in the aliphatic alcohol series is found to increase in the following order: *iso*-BuOH < *n*-BuOH < *iso*amyl alcohol < *n*-hexyl alcohol < *sec.*-octyl alcohol (Table I, Fig. 2). It is found to be increasing with the increase in the length of the aliphatic chain for all concentrations of sodium oleate. Further, it appears that the magnitude of the lowering of the interfacial tension by soap solution depends on the magnitude of the tension of the liquid against pure water, and it is found to be in the following increasing order; *iso*butyl < *n*-butyl < *iso*amyl < *n*-hexyl < *sec.*-octyl alcohol.

With potassium oleate—neutral, 10% free acid and 10% free alkali, the measurements of the iterfacial tension were carried out in the case of *iso*- and *n*-butyl alcohols. It was, however, observed that the acidity or alkalinity did not appreciably affect the results and the fundamental behaviour was the same as against sodium oleate.

FIG. 2.

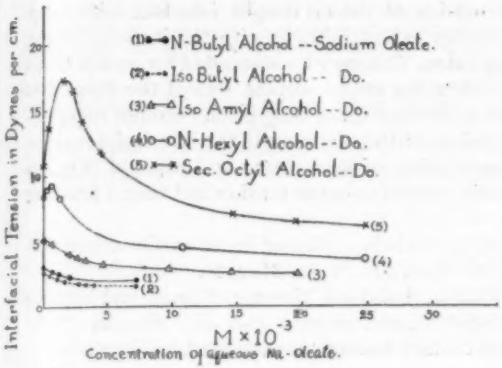
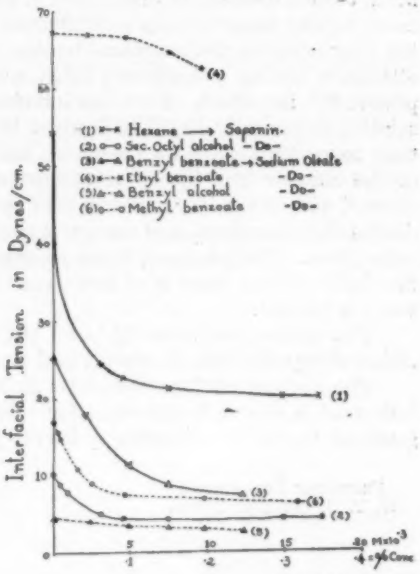

Interfacial Tension in Dynes per cm.
(1) N-Butyl Alcohol --Sodium Oleate.
(2) Iso Butyl Alcohol -- Do.
(3) Iso Amyl Alcohol -- Do.
(4) N-Hexyl Alcohol -- Do.
(5) Sec. Octyl Alcohol -- Do.
M × 10^-3
Concentration of aqueous Na-oleate.

FIG. 3.


Interfacial Tension in Dynes/cm.
(1) Hexane → Saponin.
(2) Sec. Octyl alcohol – Do–
(3) Benzyl benzoate → Sodium Oleate
(4) Ethyl benzoate – Do–
(5) Benzyl alcohol – Do–
(6) Methyl benzoate – Do–
Milo^-3
% Conc

In the case of *n*-hexyl and *sec.*-octyl alcohols, it was surprising to note that at lower concentrations of soap solutions, *i.e.*, up to $2 \times 10^{-3} M$, the interfacial tension initially increased with the increasing soap concentration and then decreased as usual with further increase in soap concentration. With saponin (Fig. 3), however, at any concentration, this rather unusual behaviour, as observed with soap solution, was not evident. Addison (*J. Chem. Soc.*, 1945, 98 ; 1944, 477) has shown that there is an almost linear relation between chain length and the surface tension of the aqueous saturated solution of normal alcohols ; but *sec.*-octyl alcohol and *tert.* -hexyl alcohol depict an irregular behaviour. It has been therefore suggested that when the structure of alcohol is altered, other factors in addition to solubility factor, might be operative. The interfacial tension curves of hexyl and *sec.*-octyl alcohols do not come under any of three types, already mentioned, as there is an initial rise of interfacial tension in very dilute solutions of soap, followed by a great lowering and thereafter the interfacial tension slowly decreasing and ultimately remaining approximately constant with increasing soap concentration.

In case of aromatic liquids (Fig. 3) it is apparent that groups $-CH_2OH$, $-COOCH_3$ and even $-COOCH_2C_6H_5$ reduce the tension against water when compared to that of unsubstituted nucleus (benzene, 34.6 dynes/cm.), while the group $-COOC_2H_5$ considerably enhances it (67.7 dynes/cm.). This surprisingly high interfacial tension of ethyl benzoate may be attributed to the peculiar effect of the ethyl group, which this group often exerts. Further, the magnitude of the surface tension lowering by sodium oleate also appears to depend on the magnitude of the tension of that liquid against water *i.e.*, greater the tension against water, greater is the lowering, but ethyl benzoate is also in this case an exception which shows much less lowering of tension against soap solution in view of its high tension against water.

In case of fatty acids, Szysykowski's equation (*Z. physikal. Chem.*, 1908, **64**, 385) expresses

the relation between the lowering of the tension and concentration of the solute. For very dilute solutions of any solute, the depression of surface tension, caused by the solute, is proportional to its concentration. As the concentration of the solute, however, increases, the lowering of the tension is no longer proportional to the concentration, but increases more slowly than does the concentration. The portions of the curves of liquids depicting interfacial tension lowering in Figs. 2 and 3, however, indicate that the lowering increases much more rapidly than the soap concentration for dilute solutions, but as the concentration of the soap increases, the interfacial tension lowering generally increases less and less slowly and ultimately reaches a nearly zero value, when further increase in the soap concentration has practically no effect. Thus the interfacial tension at the oil droplet interface with soap solution is generally found to decrease to a greater extent initially with the increase in the soap concentration and then reaches a limiting value. This may be accounted for on the basis of the unimolecular theory of adsorption; when the entire surface area of the droplet is covered with the unimolecular layer of surface active agent, the adsorption becomes independent of the concentration of the active agent, and no further decrease in the interfacial tension takes place. With hexane, these measurements using sodium oleate and saponin (Fig. 3) also indicate that there is at first a considerable reduction in the tension and then a limiting value is reached.

The unusual behaviour of hexyl and octyl alcohols is explained in an earlier communication along with that of esters (Desai and Kazi, *Curr. Sci.*, 1952, **21**, 218).

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STUDIES IN THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART III. LEAD ACETATE

By S. Aditya and B. Prasad

Cells of the type $Hg_x\ Pb_y \mid PbAc_2(c_0)\ HAc\ (c_1) \parallel$ salt bridge $\parallel Pb(NO_3)_2\ (c_0) \mid Hg_x\ Pb_y$ were studied earlier and the dissociation constant of $PbAc^+ \rightleftharpoons Pb^{++} + Ac^-$ was shown to be 3.1×10^{-3}. Study of cells of the type $Hg \mid Hg_2\ Ac_2 \parallel PbAc_2(c_0)\ HAc(c_1) \parallel$ Salt bridge $\parallel NaAc(2c_0)\ HAc(c_1)\ Hg_2Ac_2 \mid Hg$ showed that lead acetate dissociated into two stages. By combining the results of the study of the above two types of cells it was possible to calculate the two equilibrium constants. The value of $k_1(PbAc_2 \rightleftharpoons PbAc^+ + Ac^-)$ was found to be 3.0×10^{-2} and that of $k_2(PbAc^+ \rightleftharpoons Pb^{++} + Ac^-)$ to be $3{\cdot}7 \times 10^{-3}$. Study of the cells of the type in which there is no liquid junction potential $Pb_x\ Hg_y \mid PbAc_2(c_0)\ HAc\ (c_1)\ Hg_2Ac_2 \mid Hg$ showed that the calculated values of k_1 and k_2 were correct and the salt bridges had been able to eliminate liquid junction potential effectively.

In a previous communication (this *Journal*, 1952, **29**, 169) the dissociation of lead acetate was assumed to be complete at the first stage and incomplete at the second stage as shown,

$$PbAc_2 \xrightarrow{\text{complete}} PbAc^+ \rightleftharpoons + Ac^-\ Pb^{++} + 2Ac^-$$

and the dissociation constant of $PbAc^+ \rightleftharpoons Pb^{++} + Ac^-$ calculated. It was also mentioned that further work was in progress. In the present work cells of the types

(A) $Hg_x\ Pb_y \mid PbAc_2(c)\ HAc(c_1) \parallel$ salt bridge $\parallel Pb(NO_3)_2(c) \mid Pb_y\ Hg_x$ and

(B) $Hg \mid Hg_2Ac_2 PbAc_2(c)\ HAc(c_1) \mid Pb_x\ Hg_y$ have been studied.

Cells of Type (A)

Preparation and use of reversible $Hg \mid Hg_2Ac_2$ MAc electrode was reported by Larson and McDougal (*J. Phys. Chem.*, 1937, **41**, 493). Their method for the preparation of the half element was followed. In all the cells studied the concentration (g. mol./litre) of sodium acetate was twice the concentration (g. mol./litre) of lead acetate solution. Acetic acid was added both to sodium acetate and lead acetate solution used in the cell and the concentration of acetic acid in the two solutions was the same. The readings for the same concentration cell with different concentrations of acetic acid was extrapolated to zero concentration of the acid as in the previous work (*loc. cit.*). The bridge used was of the same type. In case of every cell four bridges $1oN$, $8N$, $5N$ and $4N$ were used. From these, as done in the previous work, the mean E.M.F. was calculated and used for extrapolation. The mean E.M.F. values and the extrapolated values are given in Table I (30°).

If lead acetate dissociates as

$$\begin{array}{l} PbAc_2 \xrightarrow{\text{complete}} PbAc^+ + Ac^- \\ \quad\quad\quad\

It is found that α becomes negative. So the first stage of dissociation cannot be neglected. Taking the dissociation according to the scheme,

$$\begin{array}{ccccc} PbAc_2 & \rightleftharpoons & PbAc^+ & + & Ac^- \\ (1-\beta)C & & (1-\alpha)\beta C & & \beta C \\ & & \downarrow\uparrow & & \\ & & Pb^{++} & + & Ac^- \\ & & \alpha\beta C & & \alpha\beta C \end{array}$$

the E.M.F. of the cells $Pb_xHg_y \mid Pb(NO_3)_2(c) \parallel$ bridge $\parallel PbAc_2(c)$ HAc $(c_1) \mid Pb_x Hg_y$ extrapolated to zero concentration of acetic acid and studied in Part II of this series (this *Journal*, 1952, **29**, 169) will be given by

$$E_1 = \frac{RT}{2F} \log \frac{f_{Pb^{++}} \text{ in lead nitrate}}{\alpha\beta f_{Pb^{++}} \text{ in lead acetate}}$$

and that of the cells of type (A) in this paper and extrapolated to zero concentration of acetic acid will be given by

$$E_2 = \frac{RT}{F} \log \frac{2 \times f_{Ac^-} \text{ in sodium acetate}}{(1+\alpha)\beta f_{Ac^-} \text{ in lead acetate}}.$$

From the values of E_1 and E_2 and using methods similar to that described in Part II of the series (*loc. cit.*)it was possible to calculate α and β on the basis of the assumptions that (*a*) the activity coefficient of chloride and acetate ions in two of its salts having the same ionic strength is the same, and (*b*)the activity coefficients of potassium and chloride ions in solutions of potassium chloride are the same. In Table II the values of α, β, etc. have been calculated on the basis of dissociation in two stages. The equilibrium constants are calculated as follows:

$$k_1 = \frac{a_{PbAc^+} \times a_{Ac^-}}{a_{PbAc_2}} = \frac{(1-\alpha)\beta c \, f_{PbAc^+} \, (1+\alpha) \, \beta C . f_{Ac^-}}{(1-\beta)C}$$

$$= \frac{(1-\alpha^2)\,\beta^2 C \, f_{PbAc^+} f_{Ac^-}}{(1-\beta)}$$

Here the activity of both the monovalent ions *i.e.*, $PbAc^+$ and Ac^-has been taken to be equal to that of chloride ion at the same ionic strength. Column 7 gives the values for k_1.

Further $k_2 = \frac{a_{Pb^{++}} \times a_{Ac^-}}{a_{PbAc^+}}$ which reduces itself to $k_2 = \frac{1+\alpha}{1-\alpha} . \alpha\beta C f_{Pb^{++}}$. Values of k_2 are given in Table II.

The values of k_1 and k_2 are 3.0×10^{-2} and 3.7×10^{-3} respectively. The value of k_2 obtained here(3.7×10^{-3})is very nearly its value found(3.1×10^{-3})on the basis of complete dissociation of lead acetate into $PbAc^+$ and Ac^- (this *Journal*, 1952, **29**, 174). The dissociation constant k_1 ($PbAc_2 \rightleftharpoons PbAc^+ + Ac^-$) is about ten times higher than k_2. This coupled with the fact that the value of k_2 in the paper referred to has been obtained by extrapolation to zero concentration of lead acetate explains the cause of the closeness of the two values obtained on the basis of two different pictures.

TABLE I

Conc. of HAc.	Mean E. M. F.	Extrapolated E. M. F.	Conc. of AcOH.	Mean E. M. F.	Extrapolated E. M. F.	Conc. of AcOH.	Mean E. M. F.	Extrapolated E. M. F.
	$PbAc_2$=0.01 *M*.			$PbAc_2$=0.04 *M*.			$PbAc_2$=0.075 *M*.	
0.005 *M*	0.0151 volt		0.0075 *M*	0.0239		0.010 *M*	0.0292	
0.0075	0.0146	0.0144 volts	0.010	0.02405	0.0236	0.0125	0.02945	0.0286
0.010	0.0151		0.0125	0.02410		0.0150	0.0296	
0.0125	0.0153		0.0150	0.02405		0.0175	0.02955	
	$PbAc_2$=0.02 *M*.			$PbAc_2$=0.05 *M*.				
0.005 *M*	0.0195		0.010 *M*	0.02595				
0.0075	0.0194	0.0185	0.0125	0.0266	0.0249			
0.010	0.01895		0.0150	0.02585				
0.0125	0.01885		0.0175	0.02560				
	$PbAc_2$=0.03 *M*.			$PbAc_2$=0.06 *M*.				
0.0075 *M*	0.0214		0.010 *M*	0.02825				
0.010	0.0216	0.0209	0.0125	0.02780	0.0264			
0.0125	0.0216		0.0150	0.02755				
0.0150	0.0221		0.0175	0.02745				

TABLE II

Conc.	μ in lead acetate soln.	$\beta(+1\alpha)f_{Ac}$.	$\beta(1+\alpha)$.	$\alpha\beta$.	β.	α.	k_1.*	k_2**.
0.1 *M*	0.01624	1.0105	1.1457	0.312	0.8337	0.3743	2.972×10^{-2}	4.000×10^{-3}
0.02	0.02828	0.82775	0.97017	0.2072	0.7629	0.2716	3.308	3.617
0.03	0.0396	0.72696	0.87375	0.1659	0.7078	0.2344	3.364	3.651
0.04	0.0517	0.63929	0.7815	0.147	0.634	0.2318	2.740	3.905
0.05	0.063	0.59225	0.73755	0.1300	0.6075	0.2139	2.890	3.931
0.06	0.0735	0.5518	0.69507	0.1154	0.5796	0.1991	2.902	3.783
0.075	0.0882	0.49797	0.63843	0.0878	0.5506	0.15948	2.999	3.064

*Mean value of $k_1 = 3.0\times10^{-2}$ $\quad *k_1 = \dfrac{(1-\alpha^2)\beta^2 C f_{PbAc^+} f_{Ac^-}}{(1-\beta)}$

**Mean Value of $k_2 = 3.7\times10^{-3}$ $\quad **k_2 = \dfrac{1+\alpha}{1-\alpha} a_{Pb^{++}}$

Cells of Type (B)

With a view to obtaining some more insight, cells of the type

$$Hg \mid Hg_2Ac_2PbAc_2 \text{ (c) } HAc \text{ } (c_1) \mid Pb_x\ Hg_y$$

were studied. The two half cells were filled with the same solution. Here, there is no liquid junction. The two half cells filled with the same solution were joined through a bridge containing the same solution. In lead acetate solution acetic acid had to be used and E.M.F. for zero concentration of acetic acid was found by extrapolation. The experiments were all done in duplicate and they generally agreed within 0.1 m.v. In very few cases the difference was about 0.2 m.v. The experimental data are given in Table III. In column 4 of the same table are given the extrapolated E.M.F. values for zero concentration of acetic acid.

The E.M.F. (extrapolated to zero concentration of acetic acid) of the cells of this type is given by the equation

$$E = E_0 - \frac{RT}{2F} \log a_{Pb^{++}} \times a^2_{Ac^-}$$

TABLE III
(30°)

Conc. of lead acetate.	Conc. of acetic acid.	E.M.F. (volt)	Extrapolated E.M.F. (volt)	$\beta(1+\alpha)Cf_{Ac^-}$.	$\alpha\beta Cf_{Pb^{++}}$.	$\frac{RT}{2F}\log a_{Pb}a^2_{Ac}$	E_o.
0.01 *M*	0.005 *M*	0.8326					
	0.010	0.8330	0.8320	0.01010	0.001827	0.20198	0.6302
	0.015	0.8336					
	0.020	0.8338					
0.02 *M*	0.010	0.81815					
	0.015	0.81845	0.8175	0.0164	0.00207	0.1876	0.6299
	0.020	0.81850					
	0.025	0.81880					
0.03 *M*	0.010	0.8095					
	0.015	0.8102	0.80875	0.02180	0.002265	0.1790	0.6298
	0.020	0.8104					
	0.025	0.8106					
0.04 *M*	0.015	0.8039					
	0.020	0.8043	0.8030	0.02557	0.002436	0.1739	0.6291
	0.025	0.80470					
	0.030	0.80495					
0.05 *M*	0.020	0.7796					
	0.030	0.8001	0.7990	0.02961	0.002546	0.1694	0.6296
	0.040	0.8003					
	0.050	0.8011					
0.06 *M*	0.020	0.7970					
	0.030	0.79715	0.7965	0.03311	0.002527	0.1667	0.6298
	0.040	0.7969					
	0.050	0.7970					
0.075 *M*	0.020	0.7928					
	0.030	0.7925	0.7920	0.03735	0.002220	0.1623	0.6291
	0.040	0.7930					

Mean value of E_o = 0.6296

On the basis of two stage dissociation it has been shown that $a_{Pb^{++}} = \alpha\beta Cf_{Pb^{++}}$ and $a_{Ac^-} = (1+\alpha)\beta Cf_{Ac^-}$. So the equation is reduced to

$$E = E_o - \frac{RT}{2F}\log \alpha\beta^2 (1+\alpha) C^2 f_{Pb^{++}} f_{Ac^-}.$$

The values of α and β calculated on the basis of (*i*) two stages of dissociation, (*ii*) elimination of liquid junction potential by the salt bridge, (*iii*) activity coefficient of an ion being the same in two different solutions of the same ionic strength and (*iv*) activity coefficient of acetate ion being equal to that of chloride ion in solutions of the same ionic strength, are given in Table II. With these values of α and β, E_o has been calculated and is given in Table III. The mean value of E_o is 0.6296. The difference from the mean does not exceed 0.6 m.v. This is an ample justification for the correctness of all the assumptions made by us.

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STUDIES IN THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART IV. CADMIUM NITRATE

By D. Mangaraj, S. Aditya and B. Prasad

From the E.M.F. measurement of the cell

$$Hg_xCd_y \mid \underset{(C_1)}{Cd(NO_3)_2} \parallel \text{Salt bridge} \parallel \underset{(C_2)}{Cd\ (NO_3)_2} \mid Cd_y\ Hg_x,$$

cadmium nitrate appears to be completely dissociated up to a concentration of 0.1*M*. Transport measurements as well as cryoscopic data lend support to the above conclusions.

Righellato and Davies (*Trans. Faraday Soc.*, 1930, **26**, 592) studied the conductance of cadmium nitrate and determined the dissociation constant of

$$Cd(NO_3)^+ \rightleftarrows Cd^{++} + NO_3^-$$

on the assumption that the first stage of dissociation

$$Cd(NO_3)_2 \longrightarrow Cd(NO_3)^+ + NO_3^-$$

is complete and that intermediate ion $CdNO_3^+$ has an ionic conductance of 40.

Potentiometric investigations were undertaken with the hope that they will throw some light on the nature of cadmium nitrate. The cell of the type :

$$Hg_xCd_y \mid \underset{(C_1)}{Cd(NO_3)_2} \parallel \text{salt bridge} \parallel \underset{(C_2)}{Cd(NO_3)_2} \mid Cd_xHg_y$$

was studied.

Experimental

Cadmium amalgam containing 12% of cadmium, prepared by dissolving Analar cadmium metal in mercury, distilled under vacuum, was used.

The cadmium nitrate solution was made by dissolving Analar cadmium nitrate in double distilled water. Its exact concentration was determined by analysis. The estimation was done by using oxine as a precipitant and adding excess of bromate, followed by potassium iodide and then titrating with thiosulphate (Vogel, "Quantitative Analysis", p. 455). The stock solution was kept in a closely sealed Jena bottle. From time to time its strength was checked. The other solutions were prepared from the stock solution.

The cell vessels and the bridge were of the type used previously (this *Journal*, 1951, **28**, 683). Each experiment was done in duplicate and the duplicates agreed within 0.2 m.v. For performing the duplicate experiments four half elements were required, two of which had the solution of the same concentration. The half cells having the same composition were always checked against each other. They seldom differed by more than 0.1 m.v. and if they did, they were rejected. Two half elements of different concentrations, checked as described above, were joined through a salt bridge and readings taken. All the measurements were done at 30°.

TABLE I

$Cd_xHg_y \mid Cd(NO_3)_2 \parallel$ Bridge $\parallel Cd(NO_3)_2 \mid Cd_xHg_y$

c_1 c_2

Concentrations. (g. mol./litre).	NH_4NO_3 bridge.	Recorded E.M.F.	Corrected E.M.F.	Calc. E.M.F.	Diff.
0.1 — 0.01	10 *M*	0.02140	0.02152 volt	0.012164 volt	0.12 m.v.
	5	0.02165			
0.1 — 0.02	10	0.0142	0.0143	0.014976	0.67
	5	0.0145			
0.1 — 0.04	10	0.00845	0.0086	0.008407	0.19
	5	0.0087			
0.1 — 0.06	10	0.00450	0.00455	0.004805	0.25
	5	0.00460			
0.1 — 0.08	10	0.0020	0.00195	0.00113	0.8
	5	0.0019			
0.08 — 0.01	10	0.01910	0.01925	0.01953	0.3
	5	0.01940			
0.08 — 0.02	10	0.0141	0.01415	0.0139	0.2
	5	0.0142			
0.08 — 0.04	10	0.0064	0.00655	0.0063	0.25
	5	0.0067			
0.08 — 0.06	10	0.0024	0.00245	0.00208	0.37
	5	0.0025			
0.06 — 0.01	10	0.01720	0.01725	0.01665	0.6
	5	0.01730			
0.06 — 0.02	10	0.0106	0.01065	0.01027	0.38
	5	0.0107			
0.06 — 0.04	10	0.00340	0.0035	0.00385	0.35
	5	0.00355			
0.04 — 0.01	10	0.0118	0.01185	0.01279	0.94
	5	0.0119			
0.04 — 0.02	10	0.0065	0.00665	0.0064	0.25
	5	0.0067			

The results are shown in Table I. Column 1 gives the concentrations of the two solutions of cadmium nitrate in g. mol./litre. Column 2 gives the concentration of ammonium nitrate used as the bridge solution in g. mol./litre. Column 3 gives the recorded E.M.F. Column 4 gives the E.M.F. corrected for liquid junction by Bjerrums method (*Z. physikal. Chem.*, 1905, **53**, 428). This corrected E.M.F. should be given by

$$E = \frac{RT}{2F} \log \frac{f_1 C_1}{f_2 C_2}.$$

The activity coefficient '*f*' of cadmium ion could not be calculated from the mean activity coefficient of cadmium nitrate, as has been done for lead ion in our previous work (*loc. cit.*) as no reliable data for the mean activity coefficient of cadmium nitrate exist. The activity coefficient of cadmium ion has been assumed to be equal to that of barium ion at the same ionic strength, on the basis that same valence type ion has the same activity coefficient in a solution of the same ionic strength. The activity coefficient of barium ion has been calculated from the mean activity coefficient of barium nitrate, potassium nitrate and potassium chloride. Now, having known the activity coefficient, '*E*' has been calculated and the values of E.M.F. thus obtained are given in column 5. They agree fairly well with the corrected values given in column 4. The differences are given in column 6, which shows that the difference between the observed and the calculated E.M.F. is never more than 1 m.v. So it may be taken that at least over the range of concentrations studied here, cadmium nitrate is completely dissociated.

This view is supported by the cryoscopic data (Landolt, Börnstein, Roth, Scheel, Table 1923, p. 1439) given below, which do not show any appreciable change in molecular depression up to a 0.1691 molal solution.

g. mole / 1000 g. of water	0.01997	0.4873	0.1691	1.015
Mol. depression	5.18	5.15	5.12	6.45

It gets further support from the study of transference number of cadmium ion in cadmium nitrate solution. The apparatus shown in Fig. 1 was used in the experiment to meet our need. In some experiments both silver and iodine coulometers (Fig. 2) were used and in some, only one was used. The solution in the silver coulometer was always filtered through a glass sintered crucible to collect any silver which might not be adhering to the coulometer.

FIG. 1

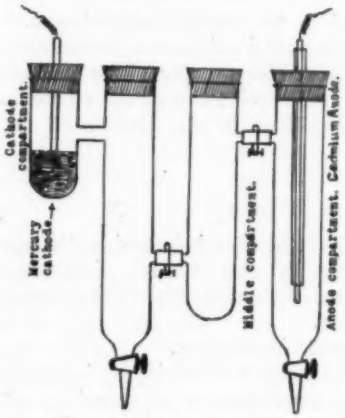
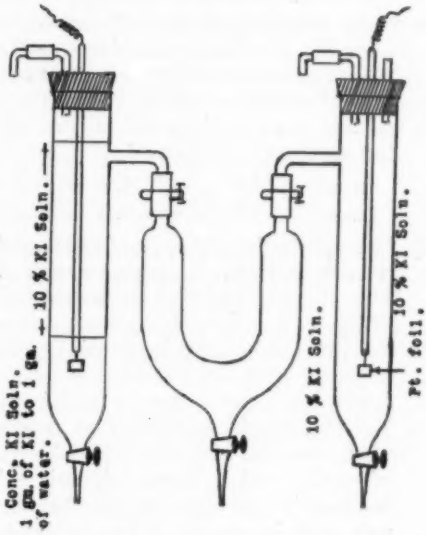


FIG. 2



Only the anode solution of the iodine coulometer was analysed. The transport number of the cadmium was calculated from the formula,

$$t^+ = 1 - \frac{\text{Increase in the number of g. equiv. of Cd in anode compartment}}{\text{g. equiv. of silver deposited or iodine liberated}}$$

when the anode solution was analysed. When the cathode solution was analysed, the formula used was

$$t^+ = 1 - \frac{\text{Decrease in the number of g. equiv. of Cd in cathode compartment}}{\text{g. equiv. of silver deposited or iodine liberated}}$$

The estimation of cadmium was done as explained earlier in this paper. The middle compartment was analysed in the case of 0.0964, 0.1839, 0.485 and 0.8491 *M* solutions and no change was recorded in the composition. The results of the experiments are given in Table II.

TABLE II

Conc. of cadmium nitrate.	Coulometer.	Compartment analysed.	Number of determinations made.	Maximum & minimum values of transference number.	Mean value of t^+.
0.01 *M*	Iodine as	Anode	3	0.4673-0.4398	0.453
0.02	well as silver	,,	3	0.4529-0.4311	0.443
0.05	,,	,,	5	0.4392-0.4143	0.425
0.10	,,	Cathode and anode, both.	7	0.4373-0.406	0.420
0.20	,,	Anode	4	0.4432-0.4128	0.435
0.35	,,	Cathode and anode both.	3	0.3904-0.3631	0.380
0.50	,,	,,	5	0.3200-0.3600	0.335
1.00			5	0.2811-0.2955	0.280
1.00	,,	Anode	3	0.2038-0.1816	0.196

Calc. transport number from $\frac{l^+(\frac{1}{2}Cd^{++})}{l^+(\frac{1}{2}Cd^{++})+l^-(NO_3^-)}$ is 0.43.

The following observations were made during the transport number experiments:

(1) Some cadmium nitrite is invariably formed in the anode compartment. The formation of this nitrite is independent of the current density at the anode, as even a change of current density by about hundred times has no appreciable effect on the amount of nitrite formed. The ratio of the gram equivalents of the nitrite formed to the gram equivalents of the silver deposited in the coulometer steadily increases with concentration.

Conc.	0.01	0.05	0.1	0.2	0.35	0.50
Ratio	0.33	0.35	0.36	0.38	0.40	0.41

(2) At concentrations up to 0.2*M* a spongy deposit of cadmium is formed on the mercury at the cathode. A small amount of nitrite is also formed simultaneously. When the concentration becomes higher, neither the spongy deposit of cadmium nor nitrite is formed in the cathode compartment.

(3) No nitrite was formed in the middle compartment in any case.

(4) A white deposit was formed at the anode. The amount of the deposit increases with increase in current density and increase of concentration of cadmium nitrate. This deposit is appreciable at concentrations greater than 0.5*M*. This deposit when dissolved in dilute hydrochloric acid oxidises potassium iodide to iodine, and when dissolved in dilute sulphuric acid, reduces permanganate. It does not give perchromic acid test. As the liberation of iodine or reduction of permanganate is only small in amount, it may be due to adsorbed nitrite.

(5) It became necessary to see if the transport number calculated from the analysis of the anode compartment was vitiated by the formation of the white deposit. So some cathode solutions in which nitrite was not formed were used for the calculation of the transport number and it was found that the same results were obtained.

(6) Some finely powdered cadmium was added to cadmium nitrate solution and it was found that appreciable amount of nitrite as well as a white deposit was formed and this amount increased with the concentration of cadmium nitrate.

The white deposit may be due to action of NO_3- on metallic cadmium. This is also given by KNO_3 as noted by a number of workers. (Mellor, "Treatise on Inorganic Chemistry"). If the nitrite formation is due to the reaction between NO_3^- and metallic cadmium, then the transference number will not be appreciably affected by the formation of the white deposit. Since the transference number is not affected in our experiment due to the white deposit, we may conclude that the white deposit is formed as a result of the interaction of metallic cadmium and nitrate ion.

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FLUOBERYLLATES AND THEIR ANALOGY WITH SULPHATES. PART VII.

COMFLEX COMPOUNDS OF FLUOBERYLLATES WITH HEXAMETHYLENE-TETRAMINE, PYRIDINE AND QUINOLINE

By Amiya Kanti Ghosh, Grihapati Mitra and Nirmalendu Nath Ray

Complex compounds of fluoberyllates of nickel, copper, cobalt and zinc with hexamethylenetetramine, pyridine and quinoline have been prepared. These complex fluoberyllates are analogous to the corresponding complex sulphates. This investigation adds further proof of the analogy of fluoberyllates to sulphates.

In continuation of the previous work on the fluoberyllates and their ammoniacal complex in which analogy between the fluoberyllates and sulphates has been established (Ray, *Z. anorg. Chem*, 1939, **241**, 165), it has now been observed that, like the sulphates, the fluoberyllates of bivalent metals, e.g. nickel, copper, zinc and cobalt, also form well defined compounds with hexamethylenetetramine, pyridine and quinoline.

Experimental

Hexamethylenetetramine Compounds

Hexamethylenetetramine-nickel Fluoberyllate.—On adding a saturated solution of nickel fluoberyllate to a saturated aqueous solution of hexamethylenetetramine at ordinary temperature and shaking, the colour of the solution faded, heat was evolved and shining pale green crystals appeared. The crystals were washed with 80% alcohol and dried in air. (Found : Ni, 13.95 ; Be, 2.31 ; N, 13.88. $NiBeF_4.C_6H_{12}N_4.7H_2O$ requires Ni, 14.31 ; Be, 2.20 ; N 13.67 per cent).

These pale green crystals are stable and soluble in water. When dried at 120°—125° it lost all its water. (Found : N, 19.38. Calc. for the anhydrous compound : N, 19.73 per cent). The anhydrous salt is yellowish green.

Hexamethylenetetramine-cobalt fluoberyllate was prepared like the corresponding nickel compounds. It forms pink coloured crystals. (Found : Co, 14.06 ; Be, 2.18 ; N, 13.56. $CoBeF_4$, $C_6H_{12}N_4$, $7H_2O$ requires Co, 14.36 ; Be. 2.20 ; N, 13.65 per cent).

It lost all its water at 120°—125°. (Found : N, 19.51. Calc. for the annydrous compound: N, 19.71 per cent).

Pyridine Complexes

2 $NiBeF_4$. 9 C_5H_5N was prepared by digesting finely powdered and dehydrated nickel fluoberyllate with pyridine on the water-bath at 80° for about 2 hours. The product was filtered through a dry filter paper, and dried by pressing between folds of filter papers and then in air. (Found : Ni, 11.47 ; Be, 1.89. 2 $NiBeF_4$. $9C_5H_5N$ requires Ni, 11.74 ; Be, 1.81 per cent).

It slowly gives off pyridine in air and is decomposed by water.

The above compound, when triturated with absolute alcohol and washed several times with the same solvent and dried as usual, was converted into $2NiBeF_4$. $5C_5H_5N$. This resembles the parent substance in properties. (Found : Ni, 16.62 ; Be, 2.57. 2 $NiBeF_4$. $5C_5H_5N$ requires Ni, 17.19 ; Be, 2.64 per cent).

The pyridine complex of the corresponding sulphates are also very unstable.

Tetrapyridine-copper fluoberyllate was prepared in the same way as the nickel compound described before. (Found : Cu, 13.59 ; Be, 1.95. $CuBeF_4 . 4C_5H_5N$ requires Cu, 13.66 ; Be, 1.94 per cent). It forms a blue unstable crystalline product.

Dipyridine-copper fluoberyllate dihydrate was prepared by adding dropwise a saturated solution of copper fluoberyllate to pyridine on a water-bath and shaking for 15 to 20 minutes. This was kept in a frigidaire until crystallised. The crystals were filtered, washed with acetone and dried in air. (Found : Cu, 18.66 ; Be, 2.53. $CuBeF_4 . 2C_5H_5N, {}_2H_2O$ requires Cu, 19.00 ; Be 2.71 per cent).

An analogous compound with copper sulphate, $CuSO_4 . 2C_5H_5N, 2H_2O$ has been described by Chang and Hü (*J. Chinese Chem. Soc.*, 1943, **10**, 113).

Quinoline Complexes

Monoquinoline-nickel fluoberyllate was prepared in the same way as described for the preceding compound. Quinoline was estimated by dissolving a weighed quantity of the compound in excess of *N*/10-HCl and the excess of the acid was titrated with *N*/10-NaOH solution (cf. Bhattacherjee and Sinha, this *Journal*, 1950, **27**, 21). (Found : Ni, 21.64 ; Be, 3.10. C_9H_7N, 46.76. $NiBeF_4 . C_9H_7N$ requires Ni, 21.50 ; Be, 3.30 ; C_9H_7N, 47.32 per cent). The compound is fairly stable in air and liberates quinoline slowly.

Quinoline-dicopper fluoberyllate was prepared in the same way as described in the copper-pyridine complex using quinoline in place of pyridine. (Found : Cu, 30.6 ; Be, 4.19. $2CuBeF_4 . C_9H_7N$ requires Cu, 29.81 ; Be, 4.23 per cent). This compound is stable in air. Chang and Yü (*Z. anorg. Chem.*, 1939, **243**, 14) obtained a corresponding compound with copper sulphate.

Triquinoline-copper fluoberyllate was prepared as above by adding quinoline dropwise to a copper fluoberyllate solution at 0°. (Found : Cu, 11.60 ; Be, 1.62. $CuBeF_4 . 3C_9H_7N$ requires Cu, 11.85 ; Be, 1.68 per cent). This compound is, however, not so stable.

Quinoline-zinc fluoberyllate tetrahydrate was prepared in the same way as that used for quinoline di-copper fluoberyllate. (Found : Zn, 18.39 ; Be, 2.57. $ZnBeF_4 . C_9H_7N, 4H_2O$ requires Zn, 18.59 ; Be, 2.57 per cent). This is fairly stable in air.

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DETERMINATION OF ALIPHATIC THIOCARBAMIDES

By R. H. Sahasrabudhey and Ranbir Singh

The volumetric determination of mono-, di-, tri- and tetra-methylthiocarbamides has been described using iodine and mercuric nitrate.

Several methods have been proposed for the determination of thiocarbamide. These depend on (*i*) desulphurisation (Volhard, *Ber.*, 1874, **7,** 100; Cuthill and Atkins, *J. Soc. Chem. Ind.*, 1937, **56,** 5T), (*ii*) oxidation of thiocarbamidic sulphur to sulphate (Cuthill and Atkins, *loc. cit.*), (*iii*) formation of the formamidine disulphide by oxidation with iodine (Reynolds, *J. Chem. Soc.*, 1903, **83,** 1; Werner, *ibid.*, 1912, **101,** 2166) and (*iv*) complex formation with mercuric nitrate (Williams, *J. Soc. Chem. Ind.*, 1939, **58,** 77T). To di-, tri and tetra-alkyl substituted thiocarbamides, which are difficultly desulphurised and oxidised (*i*) and (*ii*) cannot be satisfactorily applied. The methods (*iii*) and (*iv*), which have also the added advantage of being simple titrimetric procedures, were therefore extended to these compounds. The former is a reversible reaction ; for its quantitative completion considerable dilution is necessary which varies with the compound (vide Table I). The latter involves the formation of 1 : 1 molecular complex which is stable in aqueous solution and takes precedence in its formation over the reaction of mercuric nitrate with thiocyanate which is used as an indicator.

Experimental

Iodometric Determination.—The compounds were double crystallised from water and their purity confirmed by the melting point and estimation of nitrogen and sulphur. *M*/10 solutions were used. The iodine solution was the usual aqueous iodine, *N*/10- in potassium iodide. For every titration different quantities of thiocarbamide solution were taken in a 100 c.c conical flask and 3 c.c. starch and 2 c.c. dilute sulphuric acid solutions were added and the volume made up to 20 c.c. with water. It was then titrated with iodine as usual. The results with thiocarbamide and its methyl, dimethyl, trimethyl and tetramethyl derivatives are presented in Table I.

Table I

	Conditions				I_2 (*N*/10) consumed in case of diff. thiocarbamides (in c.c.)					
M/10 thiocarbamide soln.	H_2SO_4. (dil.)	Starch.	Water.	Total bulk.	Thi.	Me.Thi	Dime. Thi.	Trime. Thi.	Tetrame. Thi	I_2 (calc.).
10.00 c.c.	2 c.c.	3 c.c.	5.0 c.c.	20 c.c.	4.20	4.84	2.96	0.98	3.21	10.0 c.c.
5.00	2	3	10.0	20	2.58	2.96	1.90	0.55	1.87	5.0
2.50	2	3	12.5	20	1.58	1.74	1.18	0.39	1.17	2.5
1.25	2	3	13.8	20	0.95	0.99	0.72	0.28	0.72	1.25
0.62	2	3	14.4	20	0.52	0.54	0.43	0.18	0.43	0.62
0.30	2	3	14.7	20	0.28	0.28	0.24	0.15	0.24	0.30
0.20	2	3	14.8	20	0.20	0.20	0.19	0.12	0.14	0.20
0.10	2	3	14.9	20	0.10	0.10	0.10	0.09	0.10	0.10

The technique adopted by us of keeping the concentration of the indicator approximately constant by varying only the quantity of thiocarbamide in a fixed bulk of the solution (viz. 20 c.c. in the present case) has the advantage of giving sharp end-points as compared to earlier experiments where dilution was changed by increasing the bulk which must result in a lowering of the indicator : bulk ratio.

Estimation by Mercuric Nitrate.—$M/10$ solution (10 c.c.) of the thiocarbamide was taken for every titration. To this were added varying quantities of a standard $N/10$ solution of potassium thiocyanate (1 to 20 c.c.) and plain water to change dilution. Mercuric nitrate was prepared of $N/10$ concentration from metallic mercury. Ferric alum (prepared as usual in moderately concentrated nitric acid) was used as an indicator, the end-point being indicated by the disappearance of the red colour of ferric thiocyanate. Deduction of the thiocyanate equivalent of mercuric nitrate from the titre value gives the quantity of mercuric nitrate used up by the thiocarbamide. The results are presented in Table II.

TABLE II

Conditions						Volume of $N/10$ mercuric nitrate solution equivalent to thiocarbamides (corrected for the thiocyanate added in c.c.)				
$M/10$ thiocarbamide soln.	KCNS soln. ($N/10$)	Ferric alum.	Water.	Total bulk.	$Hg(NO_3)_2$ equiv. of KCNS ($N/10$)	Thi.	Me.Thi	Dime Thi.	Trime. Thi.	Tetrame-Thi.
10 c.c.	1 c.c.	2 c.c.	0 c.c.	13 c.c.	1	9.95	9.95	9.90	9.90	9.95
10	1	2	37	50	1	10.0	10.0	10.0	10.0	10.0
10	1	2	87	100	1	10.0	10.0	10.0	10.0	10.0
10	10	2	0	22	10	10.0	10.0	10.0	10.0	10.0
10	10	2	28	50	10	10.0	10.0	10.0	10.0	10.0
10	10	2	78	100	10	10.0	10.0	10.0	10.0	10.0
10	20	2	0	32	20	10.0	10.0	10.0	10.0	10.0
10	20	2	18	50	20	10.0	10.0	10.0	10.0	10.0
10	20	2	68	100	20	10.0	10.0	10.0	10.0	10.0

Symbols: Thi. denotes Thiocarbamide
Me. Thi. „ Methylthiocarbamide
Dime. Thi. „ NN-dimethylthiocarbamide
Trime. Thi. „ Trimethylthiocarbamide
Tetrame. Thi. „ Tetramethylthiocarbamide.

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REACTIONS WITH DRY ALKALINE EARTH HYDROXIDES. PART V. A SIMPLE AND RAPID METHOD FOR THE ESTIMATION OF NITROGEN, NITRIC ACID AND NITROGEN PEROXIDE CONTENTS IN METALLIC NITRATES

By J. Datta

A metallic nitrate can be estimated for its nitrogen ingredient by heating the salt with an excess of dry lime-sulphur mixture (33% or less of sulphur), titrating the evolved ammonia and estimating the same in terms of nitrate-nitrogen, nitric acid etc. In case of nitrates other than of alkali or alkaline earth metals, a preliminary treatment of the salt with Na_2CO_3 is necessary. The merits and limitations of the process have been discussed.

It has been shown in a previous communication (this *Journal*, 1952, **29**, 465) that the nitrogen of the alkali nitrate is reduced to ammonia when the salt is heated with the mixtures of any non-metal like C, S, Se, or P and any dry alkaline earth hydroxide powder ; but it is only with lime-sulphur mixture containing less than 33% sulphur that the transformation to ammonia is complete. Object of the present work was to ascertain whether the said mode of reduction could be developed into a new method for the estimation of the nitrogen ingredient of metallic nitrates. Of the different methods available for the purpose, Davarda's (*Z. anal. Chem.*, 1894, **33**, 113) probably is the most commonly used. In principle it depends upon the reduction of the nitrate to ammonia by the nascent hydrogen evolved by the action of metals like Zn etc. on aqueous solutions of caustic alkali.

Experimental

Commercial samples of the nitrates of K, Na, Ba, Pb and Cu were first dried in desiccators for 48 hours and stored in stoppered bottles. Samples from them (0.1 g.) were analysed (according to Davarda's method, cf. Treadwell and Hall, "Analytical Chemistry", Vol. II, 5th Ed., p. 384) with the results as given below under respective heads.

In the present series of experiments the mixture for the reaction (hereafter called the "charge") was prepared as follows. The accurately weighed nitrate was put into a 60 c.c. basin and pulverised by the round end of a big test tube (1×6 inches). Requisite quantities of lime and sulphur, as given in the respective heads in the tables below, were added and the whole thoroughly mixed. The test tubes for heating the charge were of hard glass and 5×1 inches in size. A mixture containing 1 g. of lime and 3 g. of $CaCl_2$ was placed at the bottom of the test tube and shaken with 5 c.c. of water. The mass was allowed to solidify and then 1 g. more of $Ca(OH)_2$ was placed over it. A glass rod (2 mm.) was centrally pressed through the mass and the charge, as made above, was poured into the annular space. The test tube was then padded on a soft cushion so as to compress the powder inside to half the volume of the test tube. The glass rod was then withdrawn with the caution to put back all the adhering solid, and the empty space of the test tube was filled up with sodalime granules (1 : 2, 20 mesh powder), plugged with double fold of filter paper, and closed with a tight fitting and seamless velvet cork having a central hole through which ($3'' \times \frac{1}{4}''$) glass tube was introduced, its other end being connected by a short rubber tubing with a long delivery tube ($2' \times \frac{1}{4}''$) dipping under standard HCl solution ($N/10$) kept in a small conical flask (60 c.c.). The test tube was arranged horizontally on a stand, the clamp fitting on the protruding portion of the cork. At first the sodalime region of the tube was heated by playing the flame, but finally placing it immediately below, in order to prevent the accumulation of any water in this region. Next, the flame of a second burner, made semiluminous and reduced to a small size, was placed about 2 inches below the region containing the charge. The test tube was occasionally rotated so as to expose all its sides to the heating action of the hot draft of air.

After about 5 minutes' slow heating the full, non-luminous flame was applied to raise the charge to a dull red heat and continued for about 5 minutes more. The flame was then carefully transferred towards the bottom of the test tube when water, expelled from the hydrated $CaCl_2$, swept away all the evolved ammonia. Finally the whole of the test tube was strongly heated by manipulating both the burners till a back suction in the long test tube indicated the complete expulsion of all the volatile matters. The delivery tube was then separated and its washings added to the contents in the conical flask, care being taken to keep the volume therein always the same (about 25 c.c.), the dilution at which the original standardisation was made. The titration of the acid furnished the alkali equivalent of the ammonia formed, wherefrom the nitrate contents, and nitrogen, nitric acid etc. could be calculated as usual. Results of the first set of experiments with nitrates as such are given in Table I. In the second set, the nitrates of Cu and Pb, as were found to yield poor results by the above treatment, were dissolved, after weighing, in 2 c.c. of hot water (60 c.c. basin being heated on the burner) and 1 g. of Na_2CO_3 added to it. The mass was stirred till almost solid. The rest of the procedure was the same as before. Results obtained from these two sets of experiments are given in Tables I and II respectively.

TABLE I

Nitrate taken.	Composition of the charge			Nitrate %	
	Nitrate.	$Ca(OH)_2$.	Sulphur.	Found.	by Davarda's.
KNO_3 ..	0.1 g	1.7 g	0.5 g	70.7	70.7
	0.2	3.4	1.0	70.2	
	0.3	5.0	1.5	68.7	
$NaNO_3$ ..	0.1	1.7	0.5 g	90.0	90.5
	0.2	3.4	1.0	90.0	
	0.3	5.0	1.5	89.1	
$Ba(NO_3)$ ..	0.1	1.7	0.5	80.0	80.0
	0.2	3.4	1.0	79.4	
$Pb(NO_3)_2$ ..	0.1	1.7	0.5	69.5	92.8
$Cu(NO_3)_2$ ..	0.1	1.7	0.5	73.2	98.4

TABLE II

	Composition of the charge			Nitrate %	
	Nitrate.	$Ca(OH)_2$	Sulphur.	Found	by Davarda's.
$Pb(NO_3)_2$ ..	0.1	1.7	0.5	92.0	92.8
$Cu(NO_3)_2$ ..	0.1	1.7	0.5	97.8	98.4

DISCUSSION

Results in Table I indicate that the nitrate contents of alkali and alkaline earth nitrates, estimated by lime-sulphur method, come to be the same as by Davarda's, but in case of other nitrates the results are appreciably lower. This is probably caused by the early thermal decomposition of the salts concerned with the loss of nitrogen as NO etc., since it has been shown (Table II) that the said salts being stabilised by the addition of Na_2CO_3, the values of the nitrate contents come almost at par with those by Davarda's. Taking this precaution in case of thermo-unstable salts, it is therefore possible to utilise the lime-sulphur method of reduction as a new process for the estimation of nitrate etc. in metallic nitrates. As compared to the standard methods, the suggested one offers several advantages: (*i*) it is finished rapidly, by skilled hand even within half an hour ; (*ii*) it does not require the use of any complicated appliances or costly material ; (*iii*) it can be undertaken in any ordinary laboratory with or without gas and water connections, since, it has been found that the use of spirit-lamp for heating and air condenser for cooling the ammoniacal vapour does not in any way interfere with the final results.

It is, however, to be noticed that the results from the lime sulphur reduction are accurate only when the weights of nitrates taken are low (preferably 0.1 g.) Even with 0.3 g. the results come about 1% lower than the standard. The cause of this is undoubtedly connected with a secondary effect, the direct reaction of sulphur and nitrate causing the loss of nitrogen in the elementary or the oxide form. The action of these very strong reactants is suppressed by the presence of $Ca(OH)_2$ (with proper adjustment of the proportions even below the limit of titrimetric detection since the yields of nitrogen as ammonia to the extent of 99 to 100% have been registered from the reduction of 0.1 g. of KNO_3, vide this *Journal*, 1952, **29**, 751) but cannot possibly be eliminated *in toto*. When, therefore, the weights of nitrates taken are high, the sum total of the effect becomes marked and registers a corresponding diminution in the yields of ammonia. This limitation of the process has therefore to be noted that it is not amenable to the use of such weights of nitrates with which N or $N/2$ standard solutions can be worked with. To one accustomed to the use of $N/10$ solutions the method offers little difficulty, dependable readings being obtained even from 0.1 g. of any nitrate

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REVERSIBILITY OF ALDOL CONDENSATION

By S. M. Gupta and S. S. Deshapande

The reversible change : acetone ⇌ diacetone alcohol is studied quantitatively and chemically by using magnesiummethyl iodide which gives methane with diacetone alcohol only. The change is catalysed by OH′ ions. At 23° and in about 10% aqueous alkaline solution the equilibrium ratio, diacetone alcohol : acetone, comes to 26 : 74.

The reversibility of aldol condensation was recognised by Koelichen (*Z. physikal. Chem.*, 1900, **33**, 1, 129) who observed that transformation of acetone into diacetone alcohol was reversible.

$$2\ (CH_3)_2.C{=}O \rightleftarrows CH_3(CH_3)C(OH)-CH_2-CO-CH_3$$

The reaction is catalysed by OH′ ions and a quantitative study has shown that the equilibrium proportion of the components is independent of their initial concentrations or that of the OH′ ions.

The change acetone ⇌ diacetone alcohol was studied by following a change in some physical property, such as (*i*) change of volume in a dilatometer (Koelichen, *loc. cit.*), (*ii*) change in refractive index (Davis and Burrows, *J. Amer. Chem. Soc.*, 1936, **58**, 311), (*iii*) heat change recorded by a specially constructed calorimeter (Sturtevant, *ibid.*, 1937, **59**, 1522).

The change can also be followed chemically provided it could be arrested when desired and a reagent is used which reacts with one of the components, quantitatively in a few seconds. In the experiments described in this paper the change was arrested by neutralising the alkali supplying OH′ ions, and the reagent was magnesiummethyl iodide which was found to evolve one molecule of methane with one molecule of diacetone alcohol, and which gave no gas with acetone. Since the change was followed in aqueous alkaline solution, it was necessary to remove water completely from the mixture of components before addition of the Grignard reagent. This was achieved by their extraction from aqueous solution by toluene and by drying the extract over anhydrous sodium sulphate. The methane evolved was measured in a Lunge nitrometer.

As the measurement of a physical property (volume) of the components was the basis of Koelichen's method, he used minimum amount of water (25 g. of a mixture of diacetone alcohol and acetone to which 1 c.c. of aqueous alkali of strength 0.2*N*, 0.1*N* and 0.05*N* was added). The value of the ratio, diacetone alcohol : acetone at equilibrium at 25°, extrapolated to 0% water, came to be 16 : 84.

In the present case the equilibrium was observed from both sides in aqueous solution by starting with one of the components in about 10% concentration (90% water) containing *N*/75 and *N*/100 alkali. The equilibrium proportion at 23° observed from either side came to 26 : 74 (average) and it was independent of the initial concentration of the component or that of OH′ ions.

Experimental

The method used for estimating diacetone alcohol by observing the volume of methane evolved by the action of Grignard reagent on a known weight of it, is the one recommended by Tschugaeff and Zerivitinoff (*Ber.*, 1907, **40**, 2027) for the determination of "active hydrogen".

The reagent was prepared by dissolving magnesium in methyl iodide diluted with pure di-*iso*amyl ether, previously distilled over sodium dust. This was introduced in the short limb of a ⅄ tube, the long limb containing the mixture of the components completely freed from water. The vertical limb of the ⅄ tube was connected through pressure tubing to the measuring tube of the Lunge nitrometer filled with brine. Air from the ⅄ tube was replaced by nitrogen bubbled through alkaline pyrogallic acid, followed by strong sulphuric acid. The ⅄ tube was dipped in a water-bath kept at 23°. By tilting, the contents in the limbs of ⅄ tube were brought together. Methane was quickly evolved and the displaced nitrogen was collected in the measuring tube of the nitrometer and its volume recorded.

The extraction of diacetone alcohol (or a mixture of it with acetone) from aqueous solution by toluene and the removal of moisture from the extract were done as follows. A definite volume of the aqueous solution (1 c.c. by a standard pipette) was poured over ammonium sulphate (1 g.) in a test tube and the resulting pasty mass was extracted thrice with 3 c.c of toluene each time. The total extract was decanted off, the ammonium sulphate was finally rinsed with 1 c.c. of toluene and the rinsing added to the extract. The total extract after drying over anhydrous sodium sulphate was transferred to the long limb of the ⅄ tube and was then brought in contact with the reagent. As will be seen from Table I, the volume of methane evolved from a certain weight of diacetone alcohol extracted from its aqueous solution is equal to the volume of the gas obtained from the same weight of the pure compound. In experiments with pure acetone and with acetone extracted from aqueous solution no evolution of gas was observed (Table I,B).

TABLE I

Wt. of diacetone alcohol.	Vol. of CH_4 evolved at N.T.P from pure compound.	Vol. of CH_4 observed at N.T.P. from the compound extracted from aq. soln.	Calc. vol.	Obs./calc.
		A. Diacetone alcohol.		
1. 0.0296	6.8 c.c.	6.8 c.c.	6.0 c.c.	1.1
2. 0.0358	7.4	7.4	6.9	1.07
3. 0.0476	10.1	—	9.3	1.08
4. 0.0636	13.1	13.1	12.3	1.06
5. 0.1000	—	20.3	19.1	1.06
		B. Acetone.		
1. 0.0358	0.0	0.0	0.0	
2. 0.0476	0.0	0.0	0.0	
3. 0.0296	0.0	0.0	0.0	

In each case the observed volume of methane is slightly higher than the theoretical. The ratio between the two (excluding case 1) varies between 1.06 and 1.08. This may be taken therefore as correction factor (Table I, A).

The experimental procedure in following the change acetone ⇋ diacetone alcohol in aqueous solution containing alkali of known strength was as follows.

One of the two components was weighed accurately in a normal flask (20 c.c.). Water was added, followed by a measured volume of normal alkali, the solution was brought to the mark and the flask left in a water-bath kept at 23°. At definite intervals 1 c.c. of the solution was pipetted out and poured over ammonium sulphate (1 g.) to which one drop of strong sulphuric acid was added to neutralise the alkali. The extraction with toluene and drying of the extract were carried out as already described,

TABLE II

Acetone.

$N/100$-Alkali (NaOH). Temp.=23°. Pressure = 750mm. Wt. of acetone for 20 c.c. = 2.0126 g. 1 c.c. = 0.1006 g.

No.	Time.	CH_4 evolved.	% Diacetone alcohol.*
1	0.0 hr.	1.9 c.c.	7.47
2	0.5	2.5	10.56
3	1.0	3.0	13.08
4	1.5	3.6	15.88
5	2.0	4.1	17.94
6	2.5	5.0	21.49
7	3.0	5.8	25.98

TABLE III

Diacetone alcohol.

Wt. of diacetone alcohol for 20c.c.=2.0082g. 1 c.c.=0.1004g. Other factors, same as in Table II.

No.	Time.	CH_4 evolved	% Diacetone alcohol*
1	0.0 hr.	20.8 c.c.	87.60
1	0.5	20.0	80.80
3	1.0	17.7	77.10
4	1.5	15.4	62.61
5	2.0	14.0	60.09
6	2.5	12.8	53.73
7	3.0	11.2	47.66
8	5.75	5.8	25.98
9	21.5	5.8	25.98

*After applying correction factor.

Tables II and III show that the same equilibrium proportion of the components, namely diacetone alcohol (26%) and acetone (74%) is reached under the experimental conditions by starting the change from either side.

TABLE IV

Acetone.

$N/75$-Alkali (NaOH).=Temp. 23°. Pressure = 750 mm. Wt. of acetone for 20c.c.=2.0104 g. 1 c.c.=0.1005 g.

No.	Time	Vol.	% Diacetone alcohol.
1	0.0 hr.	1.1 c.c.	5.14
2	0.5	1.8	7.7
3	1.5	3.3	14.48
4	2.0	4.2	13.31
5	2.5	5.1	22.63
6	2.0	5.9	25.98
7	21.0	5.9	25.98

TABLE V

Diacetone alcohol.

Weight of diacetone alcohol for 20 c.c. =2.0104 g. 1 c.c.=0.1005 g. Other conditions, same as in Table IV.

No.	Time	Vol. of CH	% Diacetoe alcohol*
1	0.0	21.4 c.c.	91.58
2	0.5	19.1	81.3
3	1.0	16.8	71.49
4	1.5	14.6	62.15
5	2.0	12.3	52.9
6	2.5	10.0	43.0
7	3.0	7.7	34.1
8	3.5	6.6	25.98

Tables IV and V show that whereas by increase in the strength of alkali from $N/100$ to $N/75$ the time required to reach the equilibrium point from the side of acetone remains unaffected. This increase favours reaching equilibrium more quickly from the side of diacetone alcohol.

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PHOTOCHEMICAL STUDIES ON URANYL SALTS

By Bal Krishna and Satyeshwar Ghosh

Under the above title, S. K. Bhattacharya and Sharda Gulvady (this *Journal*, 1952, **29**, 654) have studied the photochemical oxidation of ethyl alcohol, lactic acid and mandelic acid by uranyl nitrate. These authors have stated that the reaction is zero-molecular with respect to the aldehyde formed in each case. From a purely kinetic point of view, the idea of zero-molecularity with respect to the aldehyde formed is fictitious. This zero-molecularity will disappear if the concentration of the reductant taken is less or approximately equal to that of uranyl nitrate taken.

As a matter of fact, these authors have failed to appreciate the kinetic significance of the data obtained by them. These results clearly indicate that the reaction is zero-molecular with respect to uranyl nitrate, and as long as the concentration of the reductant is great (*i.e.* can be taken as constant) as compared to uranyl salt, the formation of aldehyde will show a zero-molecular character. In all other cases, the rate of formation of aldehyde will vary right from the beginning to the end of the reaction. The only case where the concentration of reductant is less than that of the oxidant is the first experiment of Table VII (*loc. cit.* p. 654) where the concentration of the reductant is $17.4 \times 10^{-3} M$ and that of uranyl nitrate is $20 \times 10^{-3} M$. We are sure that in this particular experiment, the $\Delta x/\Delta t$ will not show a constant character. As a matter of fact, $\Delta x/\Delta t$ in this experiment is meaningless and cannot be identified (this identification being valid in zero-molecular reaction) with the instantaneous velocity (*i.e.* dx/dt) of the reaction. This $\Delta x/\Delta t$ must be an average value, but this fact has not been mentioned by the authors.

However, there appears to be one reason which has prevented the authors from ascribing zero-molecularity to uranyl nitrate. They find that the velocity depends upon the concentration of uranyl nitrate, but they have missed the important fact that it is only the increased intensity of absorbed radiation which is material in bringing about an enhancement in the velocity of the reaction. If we keep the intensity of the absorbed radiation constant (for a particular frequency, and concentration of the reductant) and vary the concentration of uranyl nitrate, no variation in the velocity constant will be observed, *i.e.*, it will be independent of the concentration of uranyl nitrate. This fact is obvious from their data, where for the intensity of light absorbed being the same viz., 7.5×10^{-13}, the velocity constant of the reaction between lactic acid and uranyl nitrate is 7.7×10^{-10}, when the concentration of uranyl nitrate is $20 \times 10^{-3} M$ and it is 7.5×10^{-10}, when the concentration of the nitrate is halved. Consequently the reaction is zero-molecular with respect to uranyl nitrate. The total order is less than unity and greater than zero.

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